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The IJC Menomonee River Watershed Study Dispersibility of Soils and Elemental Composition of Soils, Sediments, and Dust and Dirt from the Menomonee River Watershed. Vol. 6

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The IJC Menomonee River Watershed Study

Dispersibility of Soils and Elemental Composition of Soils, Sediments, and Dust and Dirt from the Menomonee River Watershed

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques, and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

The Great Lakes National Program Office (GLNPO) of the U.S. EPA, was established in Region V, Chicago to provide a specific focus on the water quality concerns of the Great Lakes. GLNPO also provides funding and personnel support to the International Joint Commission activities under the U.S.- Canada Great Lakes Water Quality Agreement.

Several land use water quality studies have been funded to support the pollution from Land Use Activities Reference Group (PLUARG) under the Agreement to address specific objectives related to land use pollution to the Great Lakes. This report describes some of the work supported by this Office to carry out PLUARG study objectives.

We hope that the information and data contained herein will help planners and managers of pollution control agencies make better decisions for carrying forward their pollution control responsibilities.

Madonna F. McGrath
Director
Great Lakes National Program Office

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This project was in support of the U.S./Canada Great Lakes Water Quality Agreement to direct the International Joint Commission to conduct studies of the impact of land use activities on the water quality of the Great Lakes Basin and to recommend remedial measures for maintaining or improving Great Lakes water quality.

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VOLUME 6

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DISCLAIMER

This report has been reviewed by the Great Lakes National Program Office of the U.S. Environmental Protection Agency, Region V Chicago, and approved for publication. Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

PREFACE

Elemental composition (Al, Cd, Cr, Cu, Fe, Mn, Ni, P, Pb and Zn) in the sand-, silt- and clay-sized fractions of major soil types, bottom sediments, suspended sediments and dust and dirt samples from the Menomonee River Basin, Wisconsin, were analyzed. Sediments and dust and dirt samples with elemental compositions greater than levels found in the major soil types were suspected of receiving additional inputs of pollutants from sources other than soils. Locations of possible pollutant input into the Menomonee River were identified by comparing the elemental composition of the clay-sized fraction of bottom sediments. A method for estimating the dispersibility of soils was developed. Soil samples were dispersed by shaking with water to simulate natural water erosion conditions and by ultrasound to provide complete dispersion. The ratio of the amount of clay-sized particles dislodged by shaking to the amount obtained by ultrasound treatment measured the dispersibility of soils, an indirect measurement of soil erosion potential.

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I. INTRODUCTION

Concern for the effects of various land use activities on Great Lakes water quality has prompted the governments of the United States and Canada, under the Great Lakes Water Quality Agreement of April 15, 1972, to direct the International Joint Commission to conduct studies of the impact of land use activities on the water quality of the Great Lakes Basin and to recommend remedial measures for maintaining or improving Great Lakes water quality (1).

The International Reference Group on Great Lakes Pollution from Land Use Activities has implicated sediments and several elements including phosphorus (P), lead (Pb), cadmium (Cd), zinc (Zn) and copper (Cu) as contaminants of the Great Lakes. Sediments pose a serious problem to water quality and navigation. Sediments are potential carriers of pollutants--nutrients, toxic organic compounds and toxic metals--e.g., 40 to 80% of the total P load to the Great Lakes is associated with sediment (1). Accumulation of sediments in harbors of the Great Lakes requires dredging and over $100 million are spent annually to dredge Great Lakes harbors (1). The sediment loading to the Great Lakes from tributaries is about 11 million Tonnes/yr. Such large amounts of sediment reaching the Great Lakes annually indicates the need for some control measures to minimize sediment transport.

The Menomonee River Watershed was one of the six study sites in the Great Lakes basin used to evaluate the magnitude of non-point source pollution reaching the Great Lakes. The 35,200 ha Menomonee River Watershed is located in the southeastern corner of Wisconsin and discharges to Lake Michigan at the Milwaukee Harbor and carries an average sediment loading of about 10,000 Tonnes/yr. The lower portion of the Watershed--including part of the city of Milwaukee--is a commercial-industrial complex with some residential land uses. The center half of the Watershed is primarily residential with a few light industries in the City of Wauwatosa. The upper portion is mostly agricultural with scattered areas that are rapidly changing from rural to urban-residential. The Menomonee River Watershed therefore provides a situation of dynamic change in land use and serves as a focus of investigations on the effects of urban land use on water quality.

In the past, total unfractionated sediment samples have been analyzed for pollutant content and insufficient consideration has been given to the importance of particle-size distribution in evaluating pollutant carrying capacity of sediments. Using ultrasound, it is possible to maintain dispersed particles with their associated pollutants unchanged. Thus, it is possible to determine pollutant associations with particles as they appear in the field. Soils and sediments were dispersed by ultrasound into sand-, silt-, and clay-sized fractions and the elemental composition of each size fraction was determined to characterize the material and indicate possible pollutant sources. Of particular importance is the amount and elemental composition of the clay-sized frctions because most of the surface reactive sites of the

sediments are found in this fraction. A comparison of the amount and elemental composition of the clay-sized fractions of bottom sediments from different locations along the Menomonee River helps to identify those places where pollutant input occurs. The effectiveness of these depositional areas, e.g., siltation ponds, dams or harbors, can be measured in terms of the amount of clay-sized particles contained in the bottom sediments.

The dispersibility of soils is one of the factors that contributes to their erosion potential. Soils that disperse readily in water under natural conditions are considered to be more hazardous than soils that remain in an aggregated form, because dispersed fine particles stay in suspension longer and are transported more readily over land surfcaes to streams, rivers and lakes. Once reaching the river and the final receiving waterbody, they stay in suspension longer. This longer time that the particles remain in suspension longer. This longer time that the particles remainin suspension contributes to an increased biological availability of associated pollutants. Soil particles that remain intact as aggregates when subjected to the erosive force of water are more difficult to dislodge or transport over land surfaces. If they are transported into streams, the stable aggregates and their associated pollutants tend to deposit along rivers more quickly than dispersed soil particles. Dispersion of soils in the laboratory can be accomplished by shaking the soil in water to simulate a natural erosion condition or by ultrasound to provide complete dispersion of the soils. The ratio of the amount of clay-sized particles dislodged by shaking in water to the amount obtained after ultrasound treatment provides a means of evaluating soil dispersibility.

As a portion of the Menomonee River Pilot Watershed study, this investigation was designed to measure the water dispersibility of the major soil types in the Watershed and the chemical and mechanical properties of the soils (seven soil types), bottom sediments (24 sites), suspended sediments (12 sites) and urban street dust and dirt (two sites). Furthermore, attempts were made to identify sources of pollutants based on composition of clay-sized fractions and, where appropriate, to identify alternative measures for pollutant control.

2. CONCLUSIONS

Sediments are important carriers of pollutants. The Cd, Cr, Cu, Fe, Mn, Ni, Zn and P concentrations in sand-, silt- and clay-sized fractions of soils, bottom sediments, suspended sediments and urban street dust and dirt were analyzed. Sediments and dust and dirt samples with elemental composition greater than the levels found in the major soil types of the watershed were suspected of receiving additional inputs of pollutants from sources other than soils.

The Cd, Pb and Zn concentrations in some bottom- and suspended-sediment samples were found to be higher than in soils. Concentrations of these elements were correlated significantly with each other in the clay-sized fraction of sediments but not in soils. This indicates that soils were not the primary source of these metals and other sources such as vehicular emission and atmospheric fallout were major inputs.

Locations of pollutant input to the Menomonee River can be identified by comparing elemental composition of the clay-sized fractions of bottom sediments collected at different locations. Total elemental composition of unfractionated bottom sediment samples were less precise in identifying the location of pollutant input.

In an agricultural land-use area, bottom sediment samples (Dretzka Creek) with P levels greater than the soil level but without a corresponding increase in metal composition was found. In the urban area, a sediment sampling site located below the outfall of a sanitary treatment plant (STP) with secondary treatment capability (Nor-X-way-B) showed an increase in P as well as Cd, Cr, Cu, Ni, Pb and Zn levels. Clay fractions of bottom sediments from sites located below the outfall of STPs with tertiary treatment capability (River Lane and Lily Creek) showed lower levels of P as well as metals than those found at the sampling site located below an STP with secondary treatment capability. Apparently the waste water treatment for the removal of P also removed metals for the effluent.

The average P, Pb and Cd concentrations in suspended sediment samples of the Menomonee River collected during storm events were: 1840 µg/g P, 350 µg/g Pb and 1.9 µg/g Cd in the clay-sized fractions; 780 µg/g P, 180 µg/g Pb and 0.48 µg/g Cd in the silt-sized fractions; and was calculated to contain 1620 µg/g P, 290 µg/g Pb and 1.4 µg/g Cd in the unfractionated sample. The average annual storm event loadings from suspended sediments in the Menomonee River to Lake Michigan was calculated to be 16,200 kg/yr P, 3000 kg/yr Pb and 15 kg/yr Cd with about 90% of the P, Pb and Cd in the clay-sized fraction.

The Al, Fe and Mn concentrations in the clay-sized fraction of urban street dust and dirt samples were found to be lower than in the major mineral soil types of the watershed, while Cd, Cr, Cu, Ni, Pb and Zn levels were

higher. Distribution of elements into the particle-size fractions were found to divide into two main groups. One group had 78 to 87% of the metals in the sand fraction (Cr, Cu, Fe, Mn and Ni); and the other with 41 to 58% in the sand fraction (Al, Cd, P and Pb); while Zn was intermediate between these two groups (70% in the sand fraction).

The Cr, Cu, Fe and Ni concentrations in the coarse particles of the dust and dirt samples occasionally were found to be nearly equal to the concentrations in fine particles (sand vs silt and silt vs clay-sized particles). Similarly, Ni concentrations in the silt-sized fractions of suspended sediments were occasionally found to be nearly equal to the concentration in the clay-sized fraction. This may result from their presence in large particles such as metal chips from abrasion of vehicular parts or from disintegration of impervious surfaces.

Soil dispersibility--a contributing factor to soil erosion and sediment loading to waterways--was evaluated for the Menomonee River Basin, Wisconsin. Soil samples were dispersed by shaking with water to simulate natural water erosion conditions and by ultrasound to provide complete dispersion. The shaking treatment consisted of agitating a 1:10 w:v soil:water mixture for 0.5 to 128 hr. The ratio of the amount of clay-sized particles dislodged by shaking to the amount obtained by ultrasound treatment measured the dispersibility of soils. Organic carbon content (0.5 to 44%) was best correlated with soil dispersion ratio in a negative inverse relationship. If the 4 hr shaking treatment simulates the onset of soil erosion conditions in the field, as much as 90% of the primary clay-sized particles remain in silt-sized or larger aggregates during the overland transport. Thus, the amount of clay reaching the waterways can be controlled by retaining aggregates containing a high amount of clay-sized particles.

Resuspension of bottom sediments as simulated by end-over-end shaking (1 to 128 hr) was found to desorb about 0.06% Pb and 0.7% Cd of the total in the solid phase. Under extreme agitation as simulated by 15 min of ultrasound treatment, the desorption was 1.5% Pb and 2.0% Cd of the total in the solid phase. Thus, resuspension of bottom sediments to the overlying water possibly permits desorption of elements from the solid surfaces.

3. MATERIALS AND METHODS

Soil Sampling

Of the total area of the Menomonee River Watershed, 85% was mapped as soil; the remaining 15% was highly urbanized. Seven major soil types in the Watershed--representing 74% of the mapped soils--were selected: Ozaukee sil (represented 41%), Mequon sil (16%), Hochheim sil (4.0%), Pella sil (3.5%), Theresa sil (3.5%), Ashkum sicl (2.6%) and Houghton muck (3.0%). The sampling locations are shown in Fig. 1 and identified from a computerized soil survey map of the Watershed prepared by the Southeastern Wisconsin Regional Planning Commission (2). The mineral soils were sampled in the northern, rural part of the Watershed, which is more exposed to wind and water erosion than the highly-urbanized southern portion. Soil samples (top 20 to 40 cm) were taken at least 50 m away from the nearest road to minimize automobile exhaust contamination. The soil samples were dried in a forced-air dryer at 70 to 80°C, pulverized in a porcelain mortar, passed through a 10-mesh polypropylene sieve and stored in glass jars for later use.

Sediment Sampling

Bottom sediments

Whenever possible, bottom sediment sampling sites (Figs. 1 and 2) were selected near mainstem river monitoring stations and at sites subject to significant inputs of pollutants of anthropogenic origin. No samples were taken at Honey or Underwood Creeks because it was thought that the severely-modified channels would prevent the collection of representative bottom sediments. The River Lane, Nor-X-way B, Donges Bay Road, Capitol Drive and 70th Street sites were located on bedrock bottoms and samples were obtained by searching for places where sediments had been deposited. The remaining sites (County Q at the Milwaukee-Ozaukee County line, near intersection of Roads F and B, Appleton Avenue, Friestad Road, Maple Road, Menomonee Falls, Menomonee Falls Dam, Nor-X-way A, Lily Creek, Dretzka Creek, 124th Street and Dousman Ditch site Nos. 1 to 6) were located in reaches where the river flow is low or where the river widens so that flow decreases sufficiently to permit deposition of fine-textured sediments. However, in spite of the selective method of sampling for bottom sediments, meaningful data can be obtained if the samples are fractionated and the elemental composition of each particle-size fraction is determined. Clay-sized particles are the most important because of their mobility and ease of transportation over considerable distances. Except for the Nor-X-way A and Dousman Ditch site Nos. 1 to 6, all samples were taken from the mainstem of the river. The Nor-X-way A sample was taken before the confluence of an intermittent creek (Northern Crossway Creek)

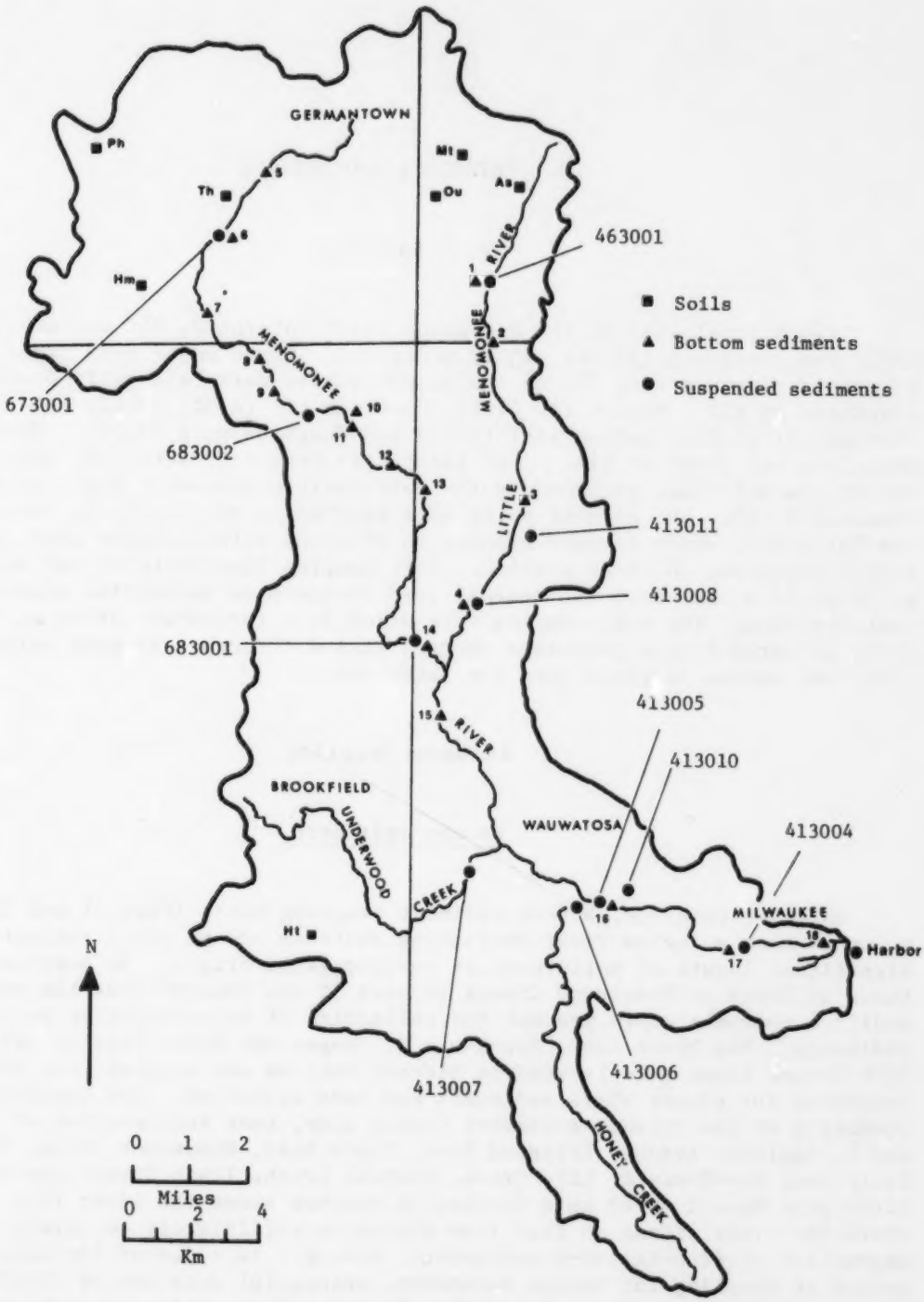

Fig. 1. Sampling sites of soils, bottom sediment and suspended sediment within the Menomonee River Watershed.

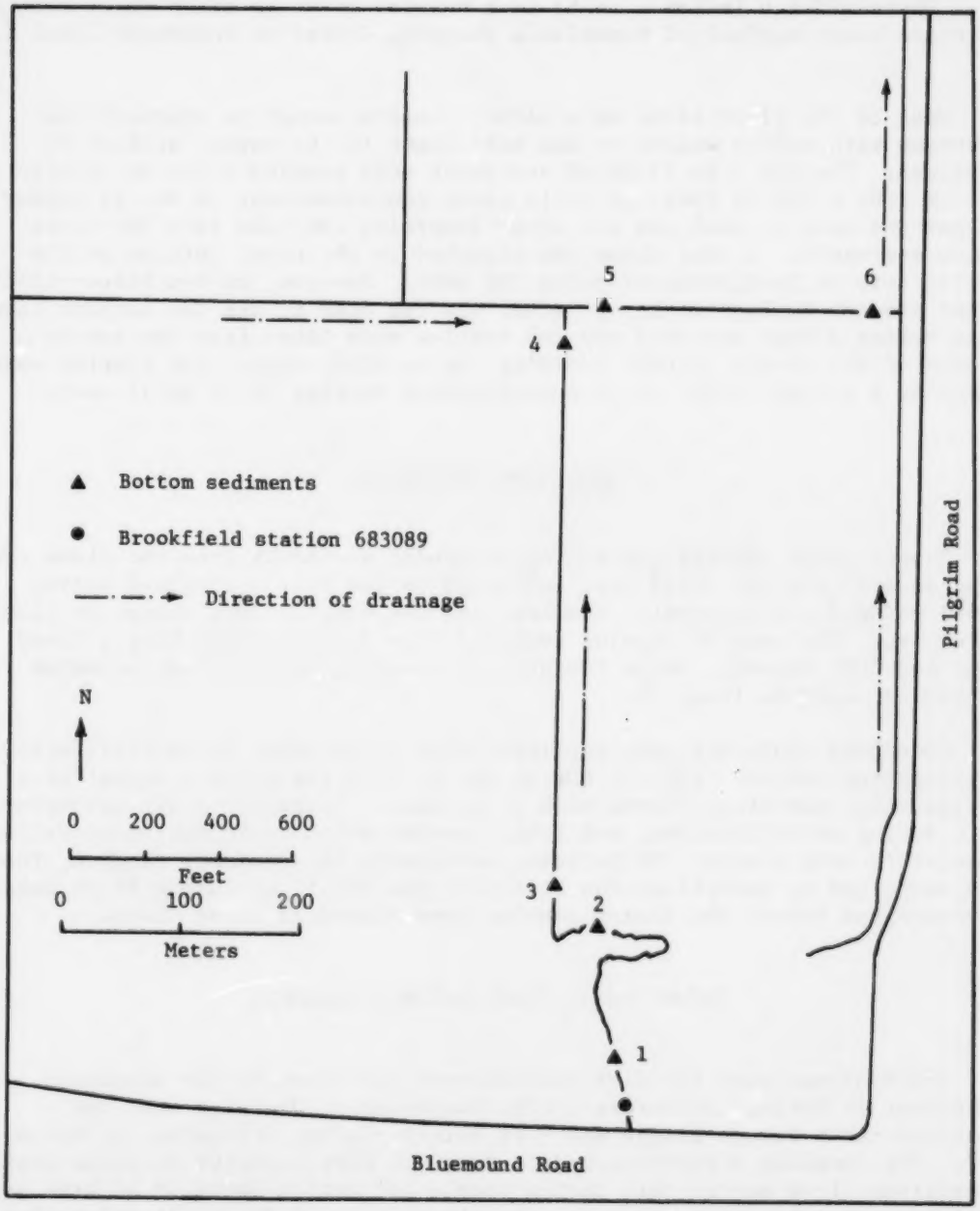

Fig. 2. Sampling sites of Dousman Ditch bottom sediments.

with the Menomonee River which drains part of Highway U.S. 41/45 and an area which constitutes about 3.9% of the area of the Menomonee River Watershed (3). Dousman Ditch (sites 1 to 6) is a natural drainage ditch which connects the storm sewer outfall of Brookfield Shopping Center to Underwood Creek (Fig. 2).

Most of the river sites were either shallow enough to approach the midstream with rubber waders or had sufficient ice to permit walking to midstream. The top 1 to 15 cm of sediments were sampled using an acrylic tube (4.5 cm I.D. x 120 cm long) to avoid metal contamination. A No. 11 rubber stopper was used to seal one end after inserting the tube into the river bottom sediments. A ring clamp was attached to the upper portion of the acrylic tube to facilitate gripping the tube. However, at two sites--124th Street and the Harbor--where the water was too deep to use the acrylic tube, a brass Eckman dredge was used and the samples were taken from the center portion of the dredge thereby avoiding the metallic edge. The samples were stored in a frozen condition in polypropylene bottles (1 L) until used.

Suspended sediments

Runoff water samples containing suspended sediments from two storm events (June 30 and July 18, 1977) were collected by the U.S. Geological Survey (USGS) using depth-integrated samples, and the samples were stored in plastic containers. The June 30 samples included only 3 sites (Falk Corp., Honey Creek and 70th Street), while the July 18 sampling included all mainstem monitoring stations (Fig. 1).

Suspended sediments were separated from river water by centrifugation in polypropylene bottles (250 ml) for 30 min at 7500 rpm using a Sorval RF-2 refrigerated centrifuge fitted with a GSA head. Temperature was maintained at 20° C during centrifugation, and those samples which could not be centrifuged immediately were frozen. To further concentrate the sediment samples, they were subjected to centrifugation at 10,000 rpm for 10 min using 50 ml Oakridge polypropylene tubes; the frozen samples were stored in these tubes.

Urban Street Dust and Dirt Sampling

Urban street dust and dirt samples were collected by the Wisconsin Department of Natural Resources (WDNR) Southeastern District from two locations--13th Street Bridge and 91st Street--during September and October 1977. The sampling sites--located in front of fire hydrants to avoid possible interference from parked cars during sample collection--were in an area not sewpt by municipl street sweepers. Sampling sites--0.91 m wide and 4.57 m along the street curb--were carefully swept three times with a portable electric vacuum cleaner and the collected samples were weighed. Whenever possible, samples were collected immediately after a rainstorm and 2 to 4 days thereafter. It should be noted that rainfall recorded at Mitchell Field Airport, Milwaukee, Wisconsin, was not necessarily the same as that occurring at the sampling sites.

Ultrasound Dispersion and Fractionation of Soil and Urban Street Dust and Dirt Samples

Samples (3 g) were placed in pre-weighed glass beakers (30 ml) and soaked overnight with enough water to submerge the sample. Although Genrich and Bremner (4) indicated that overnight soaking was unnecessary, this step was included as a precautionary measure against incomplete dispersion. After soaking the samples overnight, more water was added to approximately 30 ml and the beakers were placed in an ice bath for ultrasound treatment. The ultrasound treatment continued for 15 min at 100 to 125 watts using a Braun model 1510 ultrasonic generator with a standard probe. Preliminarly dispersion tests indicate that 15 min is sufficient to disperse the soil particles. After ultrasound treatment, the silt- and clay-sized fractions were decanted along with some sand into polycarbonate tubes (110 x 15 mm) for centrifugation. The sand fraction remaining in the beaker was rinsed several times to ensure complete removal of silt- and clay-sized particles. The silt-plus clay-sized fractions in the centrifuge tubes were resuspended and centrifuged at appropriate speed to separate the silt and sand from the clay. The silt and sand fractions were rinsed several times with distilled water, resuspended and centrifuged until the water became clear. The clay suspension was collected in 50-ml Oakridge centrifuge tubes. The particle-size fractions chosen were: Sand--2000 to 62 μm, silt--62 to 4 μm and clay--<4 μm as used by the USGS. Centrifugation time was calculated using Stoke's Law assuming a particle specific gravity of $\rho = 2.65$ for soil and $\rho = 1$ for water. For clay-sized particles (<4 μm), centrifugation time was 99 sec at 600 rpm. Usually the first two centrifugations were conducted for longer time periods and/or at higher speeds than the computed values to compensate for the increase in viscosity due to the larger amounts of clay in suspension. Additional centrifugations (1 to 3 times) were performed at the calculated time and speed. Clay suspensions were concentrated further by centrifugation at $\geq$10,000 rpm for $\geq$10 min in 50 ml Oakridge centrifuge tubes and transferred to pre-weighed beakers (30 ml) prior to drying and weighing. Sand was separated from silt by resuspending the sample and allowing for gravity settling of the sand at 26 sec for a 10 cm fall. Usually the first two partitionings of silt from sand were conducted with <10 cm fall and longer time periods. Silt particles were transferred to pre-weighed beakers (30 ml) to be dried and weighed. The remaining sand was transferred to the original pre-weighed beakers used in the ultrasound treatment which contained sand not initially decanted. Each fraction was oven-dried for $\geq$24 hr at 110° C, cooled in a dessicator and weighed. Supernates arising from fractionation of soils were collected for analysis of elements in solution. In some samples, the supernates were filtered through a 0.4 μm polycarbonate membrane filter using an all-plastic Nucleopore filter holder and were designated as filtered supernates. The second set was designated as unfiltered supernates.

"Dispersion" and Fractionation of Soil by Shaking in Water

Soil samples (1.5 g) in 15 ml deionized, distilled water were placed in glass centrifuge tubes (150 x 15 mm) with screw caps and shaken on an end-over-end shaker for 1, 4, 16, 32, 64 and 128 hr at 20 to 24 cycles/min using a Scientific Industries Inc. Multipurpose rotator. After "dispersion," the

samples were fractionated by centrifugation and gravity settling as described for ultrasound-dispersed soil samples. The supernates obtained after centrifugation were collected and stored. The samples--shaken for 1 to 16 hr--were left unfiltered, while those shaken for 32 to 128 hr were filtered through 0.4 μm membrane filters.

Ultrasound Dispersion and Fractionation of Sediments

Bottom sediments

Bottom sediments were thawed, mixed and a subsample (2 to 12 g) placed in a pre-weighed glass beaker (30 ml); a larger sample size was used if the clay content of the sediment was known to be low. The ultrasound treatment and fractionation procedure were the same as those for soil samples. Fractionated samples were oven-dried and weighed. All supernates arising from fractionation were collected and stored for analysis.

Suspended sediments

Frozen suspended sediment samples were thawed and subjected to ultrasound treatment at 80 to 100 watts for 3 min in a test tube to disperse the sediments aggregated due to high ionic strength resulting from eutectic freezing. A shorter ultrasound treatment time with lower energy was used since the suspended sediments were not as tightly-bound as the soil samples. Suspended sediment samples were transferred to polycarbonate centrifuge tubes (110 x 15 mm) and fractionated by centrifugation and gravity settling as described for soil samples. Fractionated samples were oven-dried and weighed.

Digestion of Particle-Size Fractions

After recording the weights of the dried particle-size fractions 6 to 8 ml of concentrated redistilled HNO_3 (to remove metals) were added slowly to the beakers to allow time for CO_2 evolution. The beakers were covered and heated on a hot plate (5). This procedure was adequate for soil and suspended sediment samples but not for silt- and clay-sized fractions of bottom sediments because the organic matter was more resistant to HNO_3 oxidation. In these cases, samples were treated alternately with 2 ml of redistilled 1:1 HCl and concentrated redistilled HNO_3 and were heated to near dryness prior to each new addition of acid. The digests were transferred to 30 ml plastic bottles after gravity settling of the solids. The solids were rinsed twice with deionized distilled water and the rinse water was added to the digest to bring the volume to 20 to 25 ml.

The supernates collected during the fractionation procedures were placed in 250 ml erlenmeyer flasks and digested with 3 ml concentrated redistilled HNO_3. Further digestion was continued after addition of 3 ml each of concentrated redistilled HNO_3 and redistilled 1:1 HCl.

Elemental Analysis

The metals--Cd, Cr, Cu, Ni and Pb--were analyzed by flame atomic absorption spectroscopy (AAS) using a Perkin Elmer model 603 AA Spectrophotometer. Sodium interference was sufficiently high--especially for bottom sediment samples--to require the use of the deuterium arc background corrector in a single beam mode (the Perkin Elmer model 603 does not have a double beam option when using the background corrector). Determination of Al, Fe, Mn and Zn concentrations in the digests required dilution which served to diminish salt interference. These elements were analyzed by flame AAS using a double beam mode without deuterium arc background correction on the Perkin Elmer model 306 AA Spectrophotometer. An aliquot of the HNO_3-HCl digest was used for "total" phosphorus analysis by the molybdenum blue method (5). The concentrations of Cd, Cr, Ni and Pb in the supernate obtained from dispersion of soils by shaking in water were below flame AAS detection. These elements were determined by the Perkin Elmer model 603 AA Spectrophotometer equipped with a Perkin Elmer graphite furnace model HGA 2100A. For Cd and Cr determination, 0.25 mg $(NH_4)_2(HPO_4)$ were added to 20 µl samples injected into the furnace to stabilize the volatilization temperature of Cd and to reduce the salt interference associated with Cd and Cr determination (6).

Organic carbon in soils was determined using a Leco Induction Furnace and Carbon Analyzer after removal of inorganic carbon with H_2SO_3 or HCl (7).

Elemental compositions and particle-size distributions of soils, suspended seidments and urban street dust and dirt samples were analyzed in duplicate. Bottom sediment samples were analyzed in triplicate.

4. RESULTS AND DISCUSSION

Particle-Size Distribution of Samples

The concentration of elements sorbed onto surfaces of soils, sediments and urban street dust and dirt particles tend to increase with increasing surface area. The clay-sized particles have the highest concentration of sorbed elements due to their high surface area per unit mass. Removal of the effect of different clay contents in soil, sediment and dust and dirt samples on the elemental composition of the samples can only be achieved by fractionation into sand-, silt- and clay-sized separates.

Dispersion of samples was accomplished by ultrasound treatment which allows the organo-mineral complex and their associated elements to remain intact. The commonly-used hydrogen perioxide-"Calgon" (Na-hexa metaphosphate) dispersion method was avoided because H_2O_2 destroys the organic component and alters the chemical composition of the dispersed particles while "Calgon" interferes with phosphorus determinations. Fractionation into different particle sizes was performed using the gravity settling and centrifugation techniques. This method was preferred because it approximates the conditions of particle transport and deposition better than sieving and filtration techniques. The particle-size distribution of soils, sediments and urban street dust and dirt are given in Table 1.

Using the average particle-size distribution of the six mineral soils as a reference, it can be seen that the average particle-size distribution of suspended sediment was skewed toward the clay-sized fraction as a result of the deposition of coarser materials; on average, suspended sediments contained 77% clay-sized particles compared to 27% for soils. The average particle-size distribution of the urban street dust and dirt samples was skewed toward the coarser size particles; only 5% of the particles were in the clay-sized range. The low amounts of fine particles on urban streets may result from wind and runoff transport of fine particles, leaving coarser materials behind. The average particle-size distribution of bottom sediments is difficult to determine from the data obtained because sampling sites were selected for high clay content. Some sampling sites were located on bedrock bottoms and samples were collected by searching for places where sediments had been deposited. Other sampling sites were chosen at segments of the river where it widens and flow rate decreases sufficiently to allow deposition of fine sediments.

Low amounts of clay-sized particles (2 to 14%) were found in the Milwaukee Harbor bottom sediments (8), even though river flow decreases sufficiently at the river mouth to permit sediment deposition; occasional dredging of the Harbor has been necessary because of sediment deposition. In contrast, bottom sediments from several upstream sites--in "pools" and behind

Table 1. Particle-size distribution and phosphorus concentrations in each particle-size fraction of soils, sediments and urban street dust and dirt in the Menomonee River Watershed

Sample/sampling location*	Particle-size distribution, %			Total P, µg/g		
	Sand	Silt	Clay	Sand	Silt	Clay
		Soils				
Ozaukee sil (Ou)	24	57	19	119	241	2,757
Mequon sil (Mt)	35	36	29	186	443	2,668
Hochheim sil (Hm)	29	44	27	82	154	1,821
Ashkum sicl (As)	21	44	35	491	397	2,775
Pella sil (Ph)	14	49	37	426	290	1,517
Theresa sil (Th)	22	62	16	79	128	2,336
Houghton muck (Ht)	1	38	61	302	327	503
Pooled standard deviation	2.4	2.1	1.5	19	61	206
		Bottom Sediment				
Little Menomonee River						
Donges Bay Road (1)	59	25	16	149	394	2,092
County Q Road (2)	25	25	50	404	524	1,557
Road F near Road B (3)	64	19	17	81	290	1,782
Appleton Avenue (4)	17	32	51	154	200	426
Upper Menomonee River						
Friestad (5)	36	37	27	258	561	1,434
River Lane (6)	65	19	16	108	490	1,564
Maple Road (7)	58	23	19	69	330	1,410
Menomonee Falls (8)	27	30	43	365	570	1,688
Menomonee Falls Dam (9)	16	26	58	385	404	**
Northern Crossway A*** (10)	46	19	35	216	288	888
Northern Crossway B*** (11)	67	19	14	180	894	3,529
Lily Creek (12)	21	46	33	872	1,949	4,214
Dretzka Creek (13)	30	23	47	529	700	3,115
124th Street (14)	18	45	37	641	1,839	2,943
Lower Menomonee River						
Capitol Drive (15)	46	28	26	128	210	2,203
70th Street (16)	80	8	5	141	418	1,584
Falk Corporation (17)	46	33	21	289	1,257	2,683
Harbor (18)	84	10	6	42	1,930	2,360
Pooled standard deviation	5.1	6.8	6.3	112	157	603

Table 1. Continued

Sample/sampling location*	Particle-size distribution, %			Total P, µg/g		
	Sand	Silt	Clay	Sand	Silt	Clay
Suspended Sediment+						
Little Menomonee River						
Donges Bay Road (463001)	0	9	91		760	1,795
Noyes Creek (413011)	0	6	94		286	1,109
Appleton Avenue (413008)	0	17	83		402	1,061
Upper Menomonee River						
River Lane (673001)	0	18	82		1,030	4,016
Pilgrim Road (683002)	0	19	81		1,366	2,023
124th Street (683001)	0	28	72		903	2,142
Lower Menomonee River						
Underwood Creek (413007)	0	18	82		724	1,376
Honey Creek (413006)++	1	35	64	26	300	900
Honey Creek (413006)	0	20	80		864	1,705
70th Street (413005)++	0	29	71		499	1,370
70th Street (413005)	0	18	82		640	1,414
Schoonmaker Creek (413010)	0	27	73		770	2,179
Falk Corporation (413004)++	6	54	40	350	980	2,190
Falk Corporation (413004)	0	17	83		873	1,148
Harbor	0	28	72		1,260	3,010
Pooled standard deviation	2.0	1.4	3.3	12	108	238
Urban Street Dust and Dirt						
13th Street Bridge, 9/22/77	86	9	5	79	317	713
13th Street Bridge, 9/26/77	90	6	4	100	317	730
91st Street, 9/22/77	86	8	6	120	421	883
91st Street, 9/26/77	82	12	5	39	471	934
Pooled standard deviation	1.6	1.9	0.6	12	45	110

*Numbers or letters in parentheses correspond to sampling sites shown in Fig. 1.
**No sample.
***A-before confluence; B-after confluence.
+Samples were collected on July 18, 1977 except where noted.
++Samples were collected on June 30, 1977.
Blanks indicate no data due to the absence of sand fraction.

dams--showed high contents of clay-sized particles (33 to 58%). Apparently, fine particles were trapped in the upper reaches of the river. It was believed that clay-sized particles occur in aggregates which settle in the upstream portion of the river. By the time aggregates of clay-sized particles reach the harbor, they were dispersed and remained in suspension for a longer time before depositing on the lake floor. Lake seiche and turbulence generated by ship passage and wind can facilitate scouring and resuspension of clay-sized particles in the harbor and retard their accumulation. Thus, if the Milwaukee Harbor were to function as a large flow-through lagoon to settle out fine sediments from the Watershed or from the Jones Island STP, it would not be very efficient. The ability to trap and retain clay-sized aggregates decreases with increasing distance from the source due to aggregate dispersion.

Phosphorus in Soils

Phosphorus concentration in each particle-size fraction of the seven major soil types from the Menomonee River Watershed (Table 1) were analyzed to provide an estimate of the range of P concentration. These soils comprise the majority of the surface area material that potentially can erode and contribute sediment and associated pollutants to the waterways. The soil types were scattered randomly through the Watershed so that the source of sediment could not be related to particular soil types. The six major mineral soil types showed similar average P contents in their clay-sized fractions and covered a small range of values, with an average of 2310 µg/g. The organic soil--containing 44% of organic C--was developed in a bog area where water was impounded and represents a sink for sediment and pollutants rather than a source. This soil was included for completeness sake but was not included in the data interpretation because of its low erosion potential. The P concentration in the organic soil (503 µg/g) was found to be nearly constant for all particle sizes. It was believed that the organic constituents in each particle-size fraction were largely plant material at various stages of decomposition. All seven soil sampling sites were located in cultivated fields or pastures, and their P contents may have been affected by fertilizer additions or animals.

Phosphorus concentrations in the six mineral soils were used as a reference for comparison with bottom and suspended sediments and urban street dust and dirt samples. Those samples with P levels greater than the average soil level ($\bar{X}$ = 2310 µg/g) were suspected of receiving P input from sources other than soil. Normally, P concentration in bottom and suspended sediments would be lower than the P level in soils because of leaching of P.

Phosphorus in Bottom Sediments

Phosphorus concentrations in each particle-size fraction of the bottom sediments (sampled November 1976, Table 1) were considered to be the result of long-term sediment deposition--residence time of the bottom sediments in the Menomonee River is probably several years and a "memory effect of pollutant additions" might be recorded in the sediments.

The 18 bottom sediment sampling sites were divided into three groups: namely, the Little Menomonee River (Donges Bay Road, County Q Road, Road F near B and Appleton Avenue); the Upper Menomonee River (Freistadt Road, River Lane, Menomonee Falls, Nor-X-way A and B, Lily Creek, Dretzka Creek and 124th Street); and the Lower Menomonee River (Capitol Drive, 70th Street, Falk Corporation and the Harbor--the latter two were actually part of the estuary). Bottom sediments were sampled selectively at Donges Bay, River Lane, Nor-X-way B, Capitol Drive and 70th Street sites to obtain sufficient amount of clay for P analysis because the river bottom rests on bedrock at these sites. Since clay-sized particles stay in suspension longer and are dispersed over a greater area than coarse particles, the clay-sized fraction was considered to be more uniformly distributed throughout the river system.

Phosphorus concentrations in the clay-sized fraction of the bottom sediments varied from 246 to 5529 µg/g (Table 1) due to the diverse sources of P input to the Menomonee River at different locations. Therefore, each bottom sediment sample and site must be considered separately.

The Little Menomonee River bottom sediment sampling sites were located in a predominately agricultural area (58%, ref. 9). Phosphorus concentration in the clay-sized fraction of the bottom sediment from the Donges Bay site (2092 µg/g, Table 1) was nearly equal to the average P concentration in the clay-sized fraction of the six mineral soils (2310 µg/g). This was attributed to the relative ease with which surface soils erode to the river at this site. Some sections of the river bank near the sampling site were separated from the cultivated area by only a thin 2 m grass strip; whereas, other parts were separated by a large woodlot. There was a decrease in P concentration in the clay-sized fraction of bottom sediment taken from the three sites downstream from the Donges Bay sampling site. Each of the sites was surrounded by a wooded area, with the Appleton Avenue site being the most protected, likely accounting for it having the lowest P concentration of all bottom sediments in the river system (426 µg/g) since forests and woodlots provide very little pollutant loadings.

The Upper Menomonee River drainage area had about 55% of the area in agricultural and related land use (9). Two villages (Germantown, 5500 population, and Menomonee Falls, 17,000 population) discharge ther STP effluents to the Upper Menomonee River. The Germantown STP No. 1 outfall was located between the Freistadt Rd. and River Lane sampling sites (Germantown STP No. 2 was removed from service in 1973, ref. 10). The industrial waste water received by the Germantown STP was supplied primarily from a milk processing and a metal plating plant. This STP treats approximately 380 m^3/day of water and is classified as providing advanced level treatment for P removal from pickling liquor. The final effluent was held in a 3780 m^3 sedimentation pond before being discharged into the Upper Menomonee River (10). Phosphorus concentration in the clay-sized fraction of the bottom seidments downstream from the STP outfall (River Lane) was 1560 µg/g. This value was similar to the P concentration in the clay-sized fraction of the bottom sediments located upstream, e.g., Freistad Rd.--1434 µg/g, and in the clay-sized fractions of three upstream sites of the Little Menomonee River, namely Donges Bay Road, County Q Road and Road F near B. Thus, the amount of P contributed by the Germantown STP to the bottom sediments was similar in amount to P contributed by soil eroding from agricultural land use areas in the Watershed. Average P concentrations in the clay-sized fractions of the

sediments from the upper reaches of the Menomonee River Basin (Donges Bay Road, County Q Road, Road F near B, Appleton Avewnue, Freistadt Road, River Lane, Maple Road and Menomonee Falls) was 1490 µg/g and somewhat lower than the average P concentration in the clay-sized fraction of the six major mineral soil types (2310 µg/g). These values indicate that some leaching or desorption of P occurs from the soil during its transport to and in the river system.

The Nor-X-way A bottom sediment sampling site was located in Northern Crossway, an intermittent creek before its confluence with the Menomonee River. The creek drains about 1340 ha or 3.9% of the Watershed area, and about 60% of the areas in agricultural and related land use (3,9). The drainage area includes part of the village of Germantown, the city of Mequon, and the village of Menomonee Falls as well as portions of Highway U.S. 41/45. The immediate surrounding area of this sampling site includes Highway U.S. 41/45, frontage road property and a woodlot, none of which were likely to have received P fertilizer. As with the Appleton Avenue sampling site, the P concentration in the clay-sized fraction of the Nor-X-way A bottom sediment (888 µg/g) was lower than the levels found at the upstream site and was second lowest of all sites sampled in the river system.

The Nor-X-way B sampling site was located after the confluence of Northern Crossway Creek with the Upper Menomonee River. It was located downstream from the Menomonee Falls STP No. 1 outfall and upstream from the Menomonee Falls STP No. 2 outfall (Fig. 1). A sharp increase occurred in the P concentration of the clay-sized fraction of the Nor-X-way B bottom sediment sample (5530 µg/g) which is about twice as high as the average P concentration in the clay-sized fraction of the six major soil types. It was the highest P concentration of all 18 bottom sediment sampling sites. This sharp increase in P concentration was attributed to its location downstream from the Menomonee Falls STP No. 1 outfall. The STP was old (last major modification in 1962, ref. 10) and provides a secondary level of wastewater treatment--it does not include P removal from pickling liquor. The average hydraulic loading from the STP was 640 m^3/day.

The next downstream bottom sediment sampling site (Lily Creek) was located 3 km from Nor-X-way B and receives effluent input from Menomonee Falls STP Nos. 1 and 2. However, the P concentration in the clay-sized fraction was 4210 µg/g, which was lower than that found at Nor-X-way B. This was contrary to the expected trend in P concentration since the Lily Creek site was only 3 km downstream from Nor-X-way B and located below two STP outfalls, while Nor-X-way B was below only one outfall. It was expected that Menomonee Falls STP No. 2 would add more P to the already polluted water from upstream, thereby increasing the P concentration in the sediment sample from the Lily Creek site. Both plants receive the same type of wastewater, since a common valve regulates their flow rates. The hydraulic loading at Menomonee Falls STP No. 2 was 265 m^3/day. The No. 2 plant was newer (constructed in 1969, ref. 10) and provides tertiary treatment including a settling pond for phsophate removal. Apparently STP No. 2 made little or no additional P contribution to the Lily Creek bottom sediment. The decrease in P concentrations in the clay-sized fraction of the Lily Creek bottom sediment could be explained on the basis that the effect of the No. 1 plant diminished with distance from the outfall, and this effect was not compensated for by P loading from the No. 2 plant. Although the Menomonee River resuspends, transports and disperses the

sediments from Nor-X-way B to its Lily Creek site, a difference in P concentration in the two sediment samples could be distinguished. It was concluded that lagoons and settling ponds located near the source of P input might remove P from solution by sorption and coprecipitation mechanisms and improve the water quality of the river emptying into Lake Michigan.

The next sampling site downstream from Lily Creek was Dretzka Creek located in an agricultural area. It showed an increase in P concentration in the clay-sized fraction (5120 µg/g)--although slightly lower than the level found at the Nor-X-way B site. Some P was added at this site to the already polluted sediments from upstream. After Dretzka Creek, the P concentration in the clay-sized fraction of the bottom sediments from 124th Street to the Harbor averaged 2350 µg/g i.e., levels similar to those found in the six mineral soils ($\bar{X}$ = 2310 µg/g). It was concluded that P sorption by sediment in this portion of the Menomonee River was balanced by leaching or desorption of P from particle surfaces.

The highest P concentration in the clay-sized fraction of the 18 bottom sediment samples occurred at the Nor-X-way B sampling site, located below a STP outfall which had secondary treatment capability. Phosphorus concentration in the clay-sized fractions of sediment samples from two other sites located below STP outfalls (River Lane and Lily Creek) were lower than values found at Nor-X-way B due to the tertiary treatment capability of these plants with large settling ponds for coprecipitation of P. Sediment samples with low P concentration in the clay-sized fraction were found in the upper part of the Watershed (Appleton Avenue and Nor-X-way A) which was surrounded by woodlots and in areas where little P fertilizer is used. Apparently, the land use close to the river (woodlots) had an impact on lowering the P concentration in sediments when compared with these agricultural areas in which the woodlots were absent. This reemphasizes the importance of controlling agricultural P input into rivers through proper management of land immediately adjacent to the waterways.

Phosphorus in Suspended Sediments

Suspended sediment samples were collected and analyzed to provide a measure of the immediate and transient P input into the Menoonee River. Depth-integrated water samples were taken by USGS (Waukesha Branch) on June 30, 1977--2 days after a rainstorm--and on July 18, 1977--11 days after a rainstorm. In general, P concentrations in the clay-sized fraction of the suspended sediments were dependent on site location, time of sampling as it related to position on the hydrograph, and the nature of storm event. The time of sampling varied from 1 hr before peak flow to as much as 13 hr after peak flow (Table 2). The lack of uniformity in rain intensity and duration of storms in the Watershed made it difficult to compare the composition of suspended sediment samples with each other or with bottom sediments.

Suspended sediments from the Donges Bay Road site was sampled 1.5 hr after peak flow. Phosphorus concentration in the clay-sized fraction of suspended sediment from this site (1800 µg/g, Table 1). However, P concentrations in the clay-sized fraction of the bottom sediments were generally lower than in suspended sediments at the same location possibly due

Table 2. Flow and time of sampling during collection of suspended sediment samples on June 30 and July 18, 1977 storm events*

Stations**	Major hydrograph peak***		During sampling		Fraction of peak flow sampled	Time of sampling after peak flow, hr
	Flow, cms	Time	Flow, cms	Time		
			June 30, 1977+			
Lower Menomonee River						
Honey Creek (413006)	15.9	1015	8.98	1100	0.57	1
70th Street (413005)	24.8	1020-1025	16.2	1200	0.65	2
Falk (413004)	26.9	1020-1025	16.8	0930	0.63	-1+++
			July 18, 1978++			
Upper Menomonee River						
River Lane (673001)	0.51	1320-1410	0.51	1400	1.00	0
Pilgrim Road (683002)	6.23	0315	0.79	1530	0.13	12
124th Street (683001)	5.38	0845-0955	3.40	1520	0.63	7
Little Menomonee River						
Donges Bay (463001)	0.22	0900-1040	0.20	1130	0.90	1.5
Noyes Creek (413011)	3.54	0410-0415	1.13	1030	0.32	6
Appleton Avenue (413008)	3.65	0800-0900	0.85	1500	0.23	5.5
Lower Menomonee River						
Underwood Creek (413007)	7.33	0410-0425	2.55	0930	0.35	5
Honey Creek (413006)	32.3	0445	2.83	1100	0.09	6
70th Street (413005)	66.0	0455-0505	7.79	1730	0.12	12.5
Schoonmaker (413010)	1.98	0130	0.28	0800	0.14	6.5
Falk (413004)	67.7	0455-0505	8.50	1730	0.13	12.5
Harbor	n.a.	n.a.	n.a.	1400		

*Data made available by USGS.
**STORET numbers correspond to sampling sites shown in Fig. 1.
***Data given corresponds to the major hydrograph peak; which may actually be a plateau as indicated by the time ranges.
+Storm event on June 30, 1978 occurred 2 days after last measurable precipitation.
++Storm event on July 18, 1978 occurred 11 days after last measurable precipitation.
+++Sampled before peak.
n.a. Not available.

to more extensive leaching of bottom sediments. This effect may not be obvious if the sediment composition is controlled by STP inputs. This indicates that the long term rate of P input into this portion of the river was greater than the P concentration found in the July 18 suspended sediment sample.

The Noyes Creek suspended sediment sampling site was the next site downstream from the Donges Bay Road site. This site was located in the Noyes Creek subwatershed and receives storm water runoff from a medium density residential area. Phosphorus concentrations in the suspended sediments from the residential area vary with season--because of leaf litter and grass clippings deposited on street surfaces and from fertilizer application. Phosphorus concentration in the clay-sized fraction of the Noyes Creek suspended sediment sample was 1110 µg/g, which was the second lowest concentration in the July 18, 1977, suspended sediment samples--lower than Donges Bay Road site. The suspended sediment sample with the lowest P concentration in the clay-sized fraction (1060 µg/g) occurred in the July 18 event at the Appleton Avenue site, the next site downstream from Noyes Creek. Low P contents of suspended and bottom sediments occurred at the same locations.

Suspended sediment from the River Lane site--located in the Upper Menomonee River--was sampled during peak flow (Table 2) and had the highest P concentration (4020 µg/g) in the clay-sized fraction of all suspended sediments sampled. This could be attributed to the Germanstown STP and/or an adjacent golf course. The settling pond at the Germantown STP selectively removes sediments capable of depositing in a short period of time. Sediments that remain in suspension are transported over a greater distance without significant contribution to the bottom sediment at the River Lane site. Hence, a corresponding high P concentration in the bottom sediment did not occur even though P in the suspended sediment was high. Another possibility was that the event was of sufficient intensity that sediments of high P content were removed from the settling pond of the STP and transported to the river. Downstream from the River Lane sampling site is the Pilgrim Road site, located in the village of Menomonee Falls and located above both Menomonee Falls treatment plants. Phosphorus concentration in the clay-sized fraction of the suspended sediment at the Pilgrim Road site was about half of that found at River Lane site. This difference may be due to a lower P input at the Pilgrim Road site or to a difference in sampling time (12 hr after peak flow vs. during peak flow, Table 2). Downstream from the Pilgrim Road sampling site was the 124th Street sampling site. Phosphorus concentration in the clay-sized fraction of suspended sediment at 124th Street was lower than that of the bottom sediment but slighly higher than the suspended sediment from the upstream site--Pilgrim Road. Difference in time of sampling relative to peak flow may acount for differences in P concentration of the two suspended sediments or a possible P input along the intervening waterway.

The Lower Menomonee River was in the industrial, commercial and residential area of the Watershed characterized by a higher degree of impervious area. No municipal STP outfalls are located in this portion of the river. Except for Harbor sampling site, P concentrations in the clay-sized fraction of the suspended sediments generally were lower than in soils. With only one event sample from the Harbor site, it is difficult to identify the locations of P input. Suspended sediment from the Falk site was found to be

less polluted with P than the Harbor site while the bottom sediments from these sites had similar P composition.

Suspended sediment from Honey Creek, 70th Street and Falk sites were collected on June 30 and July 18, 1977. Although the July 18 storm was more intense than the June 30 storm, the flow rate at the time of samping was greater for the June 30 sample (Table 2) because it was sampled closer to peak flow. Consequently a higher percent of coarse particles was found in the June 30 samples than in the July 18 samples (Table 1). Phosphorus concentration in the suspended sediments from the June 30 samples showed no anamolous deviation from the July 18 samples.

Average P concentrations of suspended sediment samples (June 30 and July 18) was: 1840 µg/g in clay-sized fraction; 780 µg/g in silt-sized fraction; and 1620 µg/g in unfractionated sample. Average annual event P loading from suspended sediments in the Menomonee River to Lake Michigan was calculated to be 16,200 kg/yr with 90% of P associated with the clay-sized fraction. The calculation was based on a 3 yr average of 10,455,000 kg/yr suspended solid loading from the Menomonee River to Lake Michigan (11) and assumed that the June 30 and July 18 suspended sediments were representative samples.

Phosphorus in Urban Street Dust and Dirt

Urban street dust and dirt samples were analyzed for P in each particle-size fraction to provide an estimate of P contributed by urban storm water runoff. Total solids and P concentration in the urban street dust and dirt samples were dependent on the source of particulate matter, time of sampling and location of sampling site. The 91st Street sampling site was located in a predominantly commercial-residential area in the central portion of the Watershed and is located closer to agricultural areas that is the 13th Street site. The 13th Street sampling site was located in the lower part of the Watershed in the Industrial Valley of Milwaukee and receives atmospheric fallout from the industries. The difference in surrounding land use between the two sampling sites was reflected in the amount of solids removed per curb meter and in the geometric mean suspended particulate matter concentration at each site. The 13th Street site consistently received more total solid loading than the 91st Street site (Table 3).

Phosphorus concentration in the clay-sized fraction of the dust and dirt sample from 91st Street was slightly higher than the 13th Street sample. This may result from a higher vegetation density in the 91st Street area as well as being located closer to an agricultural area. Phosphorus concentration in the clay-sized fraction of the dust and dirt samples were found to be appreciably lower than in the mineral soils and the bottom and suspended sediments.

Metals in Soils

Metal composition of each particle size fraction--sand, silt and clay--of the seven major soils of the Menomonee River Watershed were analyzed (Tables 4 and 5). They provide an estimate of the concentration of metals in the soils

Table 3. Antecedent rainfall and solid loading of urban street dust and dirt samples in 1977

Date of sample collection or rainfall	Rainfall intensity, cm/yr	Solid loading*			
		13th Street		91st Street	
		g/m^2	kg/curb km	g/m^2	kg/curb km
Sept. 12	1.30				
15	0.76				
16		169	154	82	75
17	1.02				
18	0.84				
19		34	31	8.6	7.8
22	0.08	30	27	19	17
23	0.38				
24	1.54				
26		22	20	18	17
28		18	17	4.5	4.1
30	2.64				
Oct. 1	0.66				
3		37	34	18	16
5	0.18	35	32	6.1	5.6

*Geometric mean of atmospheric suspended particulate matter is 104.4 $\mu g/m^3$ for 13th Street and 56.6 $\mu g/m^3$ for 91st Street.

Table 4. Lead, cadmium, zinc and copper concentrations in each particle-size fraction of soils, sediments and urban street dust and dirt in the Menomonee River Watershed

Sample/sampling location*	Metal, µg/g											
	Pb			Cd			Zn			Cu		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
Soils												
Ozaukee sil (Ou)	N.D.	9.5	58	N.D.	0.16	0.78	12	32	110	2.3	17	90
Mequon sil (Mt)	4.7	11	39	N.D.	0.25	0.73	12	29	64	4.0	15	82
Hochheim sil (Hm)	5.5	9.8	56	N.D.	0.11	0.35	6.9	41	192	1.8	7.3	41
Ashkum sicl (As)	9.0	14	36	N.D.	0.53	1.24	9.8	71	154	2.0	27	106
Pella sil (Ph)	9.8	10	39	N.D.	0.23	0.81	10	40	204	1.9	8.2	44
Theresa sil (Th)	N.D.	6.0	55	N.D.	0.12	0.44	10	20	345	2.1	4.8	36
Houghton muck (Ht)	N.D.	12.3	13	N.D.	N.D.	N.D.	N.D.	34	31	N.D.	17	15
Pooled standard deviation	0.66	1.1	1.9		0.10	0.08	1.2	23	88	0.37	2.7	2.2
Bottom Sediment												
Little Menomonee River												
Donges Bay Road (1)	2.5	7.3	36	0.06	0.21	1.1	8.8	42	236	2.4	8.5	48
County Q Road (2)	9.6	17	25	N.D.	N.D.	0.86	16	43	213	2.4	11	36
Road F near Road B (3)	4.1	16	65	0.06	0.45	1.6	12	80	484	1.7	8.1	48
Appleton Avenue (4)	20	21	41	N.D.	0.16	0.58	25	48	171	3.0	6.6	29
Upper Menomonee River												
Friestad (5)	4.1	7.8	25	N.D.	0.20	1.3	11	34	168	2.1	9.8	52
River Lane (6)	7.4	16	41	N.D.	N.D.	0.98	14	32	174	1.9	8.2	44
Maple Road (7)	4.8	17	44	0.02	0.13	1.1	9.7	28	181	1.5	12	44
Menomonee Falls (8)	12	18	55	N.D.	N.D.	0.54	15	34	213	3.6	7.1	38
Menomonee Falls Dam (9)	21	42	**	0.07	0.33	**	26	50	**	3.5	12	**
Northern Crossway A*** (10)	17	65	176	N.D.	0.36	1.3	32	150	695	3.1	17	64
Northern Crossway B*** (11)	32	101	512	0.08	0.72	3.2	29	153	1,390	4.1	27	149
Lily Creek (12)	36	64	438	N.D.	0.31	2.9	61	96	1,240	9.4	11.8	145
Dretzka Creek (13)	17	55	334	0.11	0.59	2.5	23	98	949	4.1	20	122
124th Street (14)	14	33	208	N.D.	0.26	1.7	26	69	637	6.7	17	85
Lower Menomonee River												
Capitol Drive (15)	32	35	115	0.19	0.44	1.8	23	50	283	6.6	13.8	108
70th Street (16)	16	92	487	0.07	0.52	3.8	37	188	849	5.7	42	110
Falk Corporation (17)	170	412	1,439	1.88	4.98	33	127	408	2,160	102	219	475
Harbor (18)	277	771	2,210	0.35	3.8	12.2	75	469	1,400	37	198	304
Pooled standard deviation	10	16	53	0.11	0.14	0.49	11	11	101	3.2	5.6	11

Table 4. Continued

Sample/sample location*	Metal, µg/g											
	Pb			Cd			Zn			Cu		
	Sand	Silt	Clay	Sand	Silt	clay	Sand	Silt	Clay	Sand	Silt	Clay
Suspended Sediment+												
Little Menomonee River												
Donges Bay Road (463001)		N.D.	43		N.D.	0.34		70	306		20	47
Noyes Creek (413011)		139	166		N.D.	0.58		218	495		41	41
Appleton Avenue (413008)		31	63		N.D.	0.37		117	328		8.3	38
Upper Menomonee River												
River Lane (673001)		N.D.	83		N.D.	2.4		692	392		29	37
Pilgrim Road (683002)		50	244		N.D.	N.D.		235	380		22	51
124th Street (683001)		60	204		N.D.	0.90		221	409		19	71
Lower Menomonee River												
Underwood Creek (413007)		348	515		N.D.	1.7		330	623		40	78
Honey Creek (413006)++		314	720		0.9	1.7	132	180	556		24	84
Honey Creek (413006)		158	333		0.81	1.4		246	619		39	76
70th Street (413005)++		339	477		1.3	2.3		214	618		42	98
70th Street (413005)		125	165		N.D.	0.88		138	297		50	70
Schoonmaker Creek (413010)		967	1,513		N.D.	4.4		2,910	3,280		50	104
Falk Corporation (413004)++	301	441	1,030	1.2	2.3	6.4	193	327	1,670	59	85	188
Falk Corporation (413004)		104	118		0.77	0.75		124	312		37	69
Harbor		363	715		1.1	4.3		2,390	1,239		531	346
Pooled standard deviation	9	26	26	0.5	0.83	0.21	46	74	101	4	22	9
Urban Street Dust and Dirt												
13th Street Bridge, 9/22/77	142	370	1,120	0.95	6.2	19	396	811	2,590	164	166	319
13th Street Bridge, 9/26/77	245	813	2,319	2.0	11	29	495	1,070	2,890	275	268	433
91st Street, 9/22/77	540	1,655	2,891	1.3	12	15	637	1,070	1,720	270	357	356
91st Street, 9/26/77	777	2,570	5,081	2.7	17	22	907	1,320	1,800	241	478	376
Pooled standard deviation	62	47	166	0.38	0.61	1.3	130	106	248	128	24	34

*Numbers or letters in parentheses correspond to sampling sites shown in Fig. 1.
**No sample.
***A-before confluence; B-after confluence.
+Samples were collected on July 18, 1977 except where noted.
++Samples were collected on June 30, 1977.
N.D. Not detected.
Blanks indicate no data due to the absence of sand fraction.

Table 5. Aluminum, iron, manganese, chromium and nickel concentrations in each particle-size fraction of soils, sediments and urban street dust and dirt in the Menomonee River Watershed

Sample/sampling location*	Metal, µg/g														
	Al			Fe			Mn			Cr			Ni		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
Soils															
Ozaukee sil (Ou)	2,460	5,970	62,400	4,280	10,000	53,100	215	647	2,610	11	17	75	7.2	9.1	49
Mequon sil (Mt)	866	7,860	50,700	10,100	18,900	56,600	191	984	1,160	9.4	14	63	8.9	15	48
Hochheim sil (Hm)	2,450	6,160	85,400	7,520	9,550	61,000	111	575	2,270	7.0	15	75	4.2	7.7	50
Ashkum sicl (As)	5,500	6,870	61,200	2,770	6,180	40,600	47	149	238	3.7	15	71	2.3	7.8	35
Pella sil (Pb)	6,580	5,680	65,500	5,210	6,270	57,100	41	323	1,300	4.2	13	96	3.2	5.0	30
Theresa sil (Th)	2,200	6,380	79,200	10,300	8,750	60,600	100	477	1,640	14	13	69	2.1	6.0	45
Houghton muck (Ht)	3,590	4,390	4,500	10,370	8,180	8,960	104	77	130	N.D.	8.6	11	N.D.	12	12
Pooled standard deviation	761	783	4,498	711	1,240	4,660	7.7	77	104	1.4	2.6	15	0.64	2.0	1.0
Bottom Sediment															
Little Menomonee River															
Dongee Bay Road (1)	1,350	5,920	43,200	2,840	8,550	55,200	137	239	499	1.9	11	43	2.4	7.0	36
County Q Road (2)	4,640	7,500	35,100	6,320	12,300	33,000	230	317	665	6.1	13	48	4.9	13	32
Road F near Road B (3)	1,160	3,660	34,200	2,320	7,760	44,300	227	939	1,170	1.3	7.1	51	**	**	**
Appleton Avenue (4)	2,370	4,430	16,500	5,110	7,720	16,600	449	651	772	3.7	6.9	21	4.2	9.0	27
Upper Menomonee River															
Friested (5)	2,000	5,610	35,860	12,200	12,600	46,700	186	206	363	3.5	10	40	2.7	9.0	35
River Lane (6)	792	4,690	26,200	2,700	8,480	37,000	256	313	479	1.6	11	43	2.3	9.3	33
Maple Road (7)	1,490	4,900	23,500	4,750	11,900	41,900	212	250	397	1.9	11	45	2.9	8.8	35
Menomonee Falls (8)	3,130	7,120	41,600	4,920	8,890	33,400	497	310	657	5.2	11	52	6.7	9.1	34
Menomonee Falls Dam (9)	2,640	5,780	**	4,810	7,620	**	315	382	**	5.0	14	**	4.5	10	**
Northern Crossway A*** (10)	3,500	7,140	24,900	4,490	8,280	20,300	203	348	587	4.0	13	35	3.8	10	26
Northern Crossway B*** (11)	1,330	4,000	29,900	3,890	13,000	52,100	189	789	1,200	3.6	26	347	**	**	**
Lily Creek (12)	2,970	5,230	38,300	7,930	11,100	47,800	377	469	321	14	25	260	15	35	235
Dretzka Creek (13)	1,840	3,250	33,800	4,410	7,280	49,100	334	741	1,080	4.0	18	198	**	**	**
124th Street (14)	2,890	5,880	41,300	8,850	12,800	44,700	457	599	361	7.2	17	115	11	44	204
Lower Menomonee River															
Capitol Drive (15)	1,300	3,600	34,600	3,080	6,650	40,000	343	942	1,540	3.4	16	151	**	**	**
70th Street (16)	1,470	8,890	42,900	3,310	15,800	50,840	185	560	722	2.9	18	139	3.7	16	63
Falk Corporation (17)	4,500	8,210	34,600	11,800	23,100	46,900	325	704	903	40	303	329	21	62	117
Harbor (18)	**	**	**	6,550	25,100	48,100	194	706	894	12	140	556	6.2	33	83
Pooled standard deviation	492	594	5,590	1,510	4,470	7,390	64	31	111	6.0	18	84	2.7	2.7	6.9

Table 9. Continued

Sample/sampling location*	Metal, µg/g: Al			Fe			Mn			Cr			Ni		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
Suspended Sediment+															
Little Menomonee River															
Burgess Bay Road (663001)		12,200	52,500		13,200	49,700		323	768		27	59		48	45
Hoyes Creek (613011)		13,960	60,400		14,500	39,400		655	578		51	49		167	54
Appleton Avenue (613008)		8,610	42,900		11,300	35,600		503	613		16	47		33	53
Upper Menomonee River															
River Lane (673001)		12,00	37,800		136,000	50,300		528	1,620		**	45		**	34
Pilgrim Road (683002)		11,000	63,700		11,000	44,500		846	1,020		21	63		97	59
124th Street (683001)		7,700	48,500		11,800	46,400		480	783		23	154		36	79
Lower Menomonee River															
Underwood Creek (613007)		12,800	51,100		19,000	50,500		447	767		39	77		78	54
Honey Creek (613006)***	3,180	10,610	47,600	7,600	15,000	46,600	330	379	683	N.D.	25	56	54	12	52
Honey Creek (613006)		11,650	58,800		14,900	46,100		438	558		36	105		40	53
70th Street (613005)***		13,800	52,400		16,600	44,600		805	581		N.D.	51		41	70
70th Street (613005)		9,210	40,700		13,700	39,100		438	604		28	104		32	52
Schoonmaker Creek (613010)		15,000	60,900		161,000	163,000		903	806		28	98		33	65
Falk Corporation (613004)***	3,700	6,890	93,000	11,100	19,900	98,900	441	596	1,830	33	59	181	12	25	66
Falk Corporation (613004)		9,670	33,400		12,000	25,500		551	526		28	57		26	51
Harbor		20,700	53,600		145,000	68,300		817	1,640		96	239		148	140
Pooled standard deviation	890	2,405	6,681	1,493	5,574	5,395	46	68	284	36	9.4	13	5.2	6.7	9.3
Urban Street Dust and Dirt															
13th Street Bridge, 9/22/77	3,186	5,560	15,410	45,980	34,310	43,940	283	332	614	33	43	87	37	57	75
13th Street Bridge, 9/26/77	2,900	6,170	16,790	63,340	47,360	55,490	348	437	764	41	53	108	66	64	73
91st Street, 9/22/77	1,520	8,600	32,160	69,730	49,880	65,540	439	770	1,090	53	43	72	49	69	76
91st Street, 9/26/77	1,640	8,550	28,000	57,070	67,750	77,860	554	790	1,310	27	44	80	67	80	82
Pooled standard deviation	809	2,405	4,480	1,490	5,570	5,390	46	68	284	6.8	5.4	11	13	7	5

*Numbers or letters in parentheses correspond to sampling sites shown in Fig. 1.
**No sample.
***A-before confluence; B-after confluence.
+Samples were collected on July 18, 1977 except where noted.
++Samples were collected on June 30, 1977.
N.D. Not detected.
Blanks indicate no data due to absence of sand fraction.

subject to erosion in the Menomonee River Watershed. These values were used for comparison with bottom and suspended sediments and urban street dust and dirt. The clay-sized fraction was the most important fraction for this comparison because of its large surface area per unit mass on which surface sorption and desorption of metals might occur. It was expected that metal concentrations in sediments would be lower than the levels found in soils because of leaching during resuspension, transport and deposition by storm water runoff and in waterways. Furthermore, Fe and Mn may undergo chemical reduction and dissolution in an aqueous environment, thereby lowering their concentrations in sediments as compared to surface soils. Sediments with higher metal concentrations in the clay-sized fraction than found in the clay-sized fraction of soils were suspected of receiving pollutant input from external sources. However, the high concentrations of Al, Fe and Mn in the six mineral soils tend to mask other sources of these metals in sediments.

Metals in Bottom Sediments

Metal compositions for each particle-size fraction of bottom sediments are given in Tables 4 and 5. Cadmium, Cr, Cu, Ni, Pb and Zn concentrations in the clay-sized fractions of bottom sediments from the Little Menomonee River were low compared to concentrations in bottom sediments from the Upper and Lower Menomonee River and the six mineral soils (Tables 4 and 5). A similar trend also was indicated in the silt-sized fractions for some of the metals. Low metal concentrations in the clay-sized fraction of bottom sediment samples from the Little Menomonee were probably due to the predominantly agricultural and related land use in the drainage area at these sites (58%, ref. 9); Little or no industrial surface water discharge occurs into the Little Menomonee River. Except for bottom sediments sampled at Road F near B the other samples collected in the Little Menomonee River were considered to be unpolluted with respect to Cd, Cr, Cu, Ni, Pb and Zn. The metal contents of these samples were used as a basis for comparison with other bottom sediment samples.

Bottom sediment samples from the Road F near B site had higher Cd, Mn, Pb and Zn concentrations than bottom sediments from other Little Menomonee sites. However, no measurable increase in Cr, Cu and Ni concentrations was found at the Road F near B samping site. Increases in Cd, Pb and Zn concentrations at this site could be attributed to its close proximity to two well-traveled county roads. The Pb presumably was from use of leaded gasoline, the Zn from vulcanized rubber tires and oil lubricant and the Cd as an impurity of Zn (12,13).

The Upper Menomonee River subwatershed had about 55% of the land in agricultural and related land use (10). The bottom sediment at the uppermost sampling site in this subwatershed--Freistadt Road--was surrounded by agricultural land. Cadmium, Cr, Cu, Pb, Ni and Zn concentrations in the clay-sized fractions were similar to the levels found in the "unpolluted" bottom sediment samples from the Little Menomonee River. Downstream from the Freistadt Road sampling site was the River Lane site, located below the Germantown STP No. 1 outfall and adjacent to a golf course. No measurable increase in Cd, Cr, Cu, Pb, Ni and Zn concentrations occurred in the bottom sediments even though the Germantown STP No. 1 receives wastewater from a metal plating company. Low metal concentrations also were found in the clay-

sized fractions of bottom sediments from the Maple Road and Menomonee Falls sites--both located downstream from the River Lane site. Thus, bottom sediments from the four uppermost sampling sites (Freistadt Road, River Lane, Maple Road and Menomonee Falls) also were considered to be "unpolluted" with respect to Ca, Cr, Cu, Ni, Pb and Zn. Metal concentrations in the clay-sized fraction of the "unpolluted" bottom sediments showed similar ranges even though their clay-sized fraction contents varied from 14 to 51% (Table 1) and the sampling sites extended a distance of 24 km along the Upper Menoonee River and the Little Menomonee River. Metal concentrations in the clay-sized fractions of the bottom sediment samples were unaffected by clay content even though some samples were collected selectively to obtain high clay content.

The Nor-X-way A bottom sediment sampling site was located in the Northern Crossway intermittent creek, just before its confluence with the Menomonee River. It receives storm water runoff from a frontage road and U.S. Highway 41/45 which is about 100 m upstream. Except for Pb and Zn, the metal concentrations in the clay-sized fraction of the bottom sediments were similar to the "unpolluted" bottom sediment samples from the four Upper Menomonee River sites and three Little Menomonee River sites. This was also the case for the Road F near B site, which was located in close proximity to well-traveled roads and showed an increase in Pb and Zn concentrations in the clay-sized fractions of the bottom sediments as compared to the background bottom sediment samples. A slight increase in Cu concentration may have occurred above the background level at Nor-X-way A. A possible source of Cu to this site is direct industrial surface water discharge to the creek--an outfall is located upstream from the sampling site. Further analyses would be necessary to establish positively the possible increases in Cu levels and to reveal the source. The sediment sample from the Nor-X-way A site was considered to be polluted with Zn and Pb.

The village of Menomonee Falls had two STPs that discharged effluent into the Menomonee River. The first STP was located upstream from the Nor-X-way B site which was located immediately after the confluence of the intermittent Northern Crossway Creek and Menomonee River (Fig. 1). The second STP outfall was located about 3 km downstream from STP No. 1, below the Nor-X-way B and above the Lily Creek sites. In addition to domestic sewage, these plants treat wastewater from metal foundries and electroplating plants. Both plants received the same type of wastes because they have a common valve that regulated flow rates. Menomonee Falls STP No. 1 had secondary treatment capability while STP No. 2 had tertiary treatment capability. Cadmium, Cr, Cu, Pb and Zn concentrations in the clay-sized fraction of the bottom sediments from the Nor-X-way B site were significantly higher (2 to 10 times) than the "unpolluted" sites. Furthermore, they were higher than the Lily Creek sample which was downstream from Nor-X-way B and received discharges from both treatment plants. As with P concentration, the Nor-X-way B site had the highest concentrations of Cr, Cu, Ni, Pb and Zn of any site in the uppr reaches of the Menomonee River down to 70th Street. It also had the second highest Cd concentration in the clay-sized fraction of this portion of the Menomonee River. It was concluded that the level of sanitary treatment was responsible for the observed differences in P and metal concentrations in the bottom sediments. The Menomonee Falls STP No. 2 with teritary treatment for the removal of P by co-precipitation also removed metals from the effluent. The clay-sized fraction of the bottom sediments could be used to distinguish the extent of pollutant loading at these two sites which were 3 km apart, even

though the river transports and diffuses the pollutants from the Nor-X-way B site downstream to the Lily Creek site. The portion of the Menomonee River from Dretzka Creek to 70th Street did not receive continuous sewage discharge even though an overflow bypass was located at the village of Butler just upstream from the 124th Street site which occasionally discharged raw sewage into the river (10). Since this segment of the river did not receive industrial or municipal wastewater discharge, a general decline in Cd, Cr, Cu, Ni, Pb and Zn concentrations in the clay-sized fraction of the sediments was observed with increasing distance from the Nor-X-way B site to the Capitol Drive site. The slight increase in P concentration in the clay-sized fraction of Dretzka Creek bottom sediment without a corresponding increase in metal concentrations indicated an agricultural input of P rather than industrial or municipal sewage discharge. The occasional discharge of raw sewage at the village of Butler did not measurably affect metal concentrations in the clay-sized fraction of the bottom sediments from 124th Street. The level of pollutant input may have been too low or the duration of the discharge was insufficient to change the elemental composition of the bottom sediments. However, the general decline in metal contents downstream from this point never decreased levels to those found in the upper reaches of the Menomonee River.

Normally a decrease in metal concentration was expected in the bottom sediment at the Capitol Drive sampling site because is was located after the confluence of the Upper Menomonee River and the Little Menomonee River (Fig. 1). Thus, there should be evidence of a dilution effect on the metal composition of the bottom sediments particularly since bottom sediments from the Little Menomonee River were found to be "unpolluted." Furthermore, the site was located at a greater distance from the Menomonee Falls STP. However, the clay-sized fraction of the bottom sediment sampled at Capitol Drive showed an increase in Cd, Cr, Cu and Mn over the levels found at the 124th Street site. Therefore, it was suspected that another source for these metals existed. It is generally difficult to interpret slight changes in Al, Fe and Mn concentrations in bottom sediment samples because Eh and/or pH changes in the aquatic environment might influence the concentrations of these elements. However, the increase in Mn concentration in the Capitol Drive sample was quite large. It had been reported (10) that an electroplating company had one of its wastewater discharge outfalls leading directly to the Menomonee River about 1.6 km upstream from the Capitol Drive site and about 1 km downstream from the 124th Street site. In each of the three sampling surveys taken by the WDNR and Southeastern Wisconsin Regional Planning Commission (SEWRPC) from April 1973 to August 1974 (10), the concentration of Cd, Cr and Pb in the plant's wastewater discharge were found to be in excess of the maximum concentrations recommended for surface water supporting fish and other aquatic life. Other metals used by the electroplating company included Cu and Ni. Thus, three of the five metals (Cd, Cr and Cu) that were discharged by this company to the river showed increased concentrations in the clay-sized fraction of the bottom sediment sampled 1.6 km downstream from the outfall--Capitol Drive--as compared to an upstream site--124th Street. However, as of June 1975, the plating company claimed to have stopped discharging wastewater directly into the Menomonee River (14). This indicates either that a "memory effect" for metals is present in the sediments and/or other sources of metals are present. Several other industrial surface discharge sites leading to the Menomonee River in this area have been reported (10).

The next site downstream from Capitol Drive is 70th Street, which showed an increase in Cd, Cr, Pb and Zn concentrations in the clay-sized fractions of the bottom sediments. This section of the river traverses an industrial park in the city of Wauwatosa and receives water from Underwood and Honey Creeks. The Underwood and Honey Creek subwatersheds include some heavy industries which may contribute to pollutant loading at the 70th Street site. The traffic density and surface imperviousness of these subwatersheds increased as the river approached the inner city of Milwaukee. Sources of metal pollutants are diverse, although automobiles are generally important contributors of Pb from leaded gasoline; Zn from oil lubricants and vulcanized rubber; Cd as an impurity in Zn; and Ni from corrosion of Ni-containing parts (11,12,15). A sharp increase in metal concentrations in the clay-sized fraction of bottom sediments was observed at the Falk and Harbor sites, located downstream from 70th Street. Both of these sites were in the Industrial Valley of the city of Milwaukee and receive storm water runoff from a railroad yard, chemical plants, foundries and interstate highway 94. The Harbor site showed an increase in Cr and Pb and a decrease in Cd, Cu, Ni and Zn concentrations in the clay-sized fraction of the bottom sediment as compared to the Falk site. However, these differences in the bottom sediments may not represent actual differences in pollutant input from surface discharges due to disturbance of the sediments. The Harbor site was located in that part of the river used by ships and was dredged by the Army Corps of Engineers. The most recent dredging operation--performed in 1975--may have affected the metal concentrations in the Harbor sediment sample. Both sites were located in the estuary part of the river and were affected by lake seiche.

Elemental composition of clay-sized fractions of bottom sediments were found to be useful in identifying possible sites of pollutant input. These values were compared with values found in the major mineral soil types of the Watershed. The elemental composition of soils was expected to be higher than "unpolluted" bottom sediments due to leaching and/or desorption of elements from particle surfaces. Metal concentrations in the clay-sized fraction of bottom sediments that were greater than levels in "unpolluted samples" were considered to have received metal inputs from sources other than soils.

In agricultural land use areas, bottom sediments with P levels greater than the soil levels but without a corresponding increase in metal levels were found. In urban areas, sediments which received effluent from a STP with secondary treatment capability showed an increase in Cd, Cr, Cu, Ni, P, Pb and Zn concentrations. Sediment samples from the inner city and Industrial Valley of Milwaukee have high metal concentrations presumably from atmospheric fallout and storm water runoff, since there are no STP outfalls in this segment of the river. The Al, Fe and Mn concentrations in "unpolluted" bottom sediment samples were slightly lower than those found in soils.

Metals in Dousman Ditch Bottom Sediments

Oftentimes, sediments that are transported from a subwatershed to a receiving body of water traverse through natural drainage ditches or marshes where sediments are trapped. The Brookfield Shopping Center specific study site was chosen to evaluate such an effect. It had a storm sewer outfall which was connected to Underwood Creek by a natural drainage ditch

(Dousman Ditch) and traverses through a bog. Location of bottom sediment sampling sites are shown in Fig. 2 and the particle-size distribution and elemental composition of each particle-size fraaction are given in Table 6. The Mn concentration was found to be lower than the soil level for bottom sediments. The high organic matter content of the bottom sediment and the surrounding muck soil likely contributed to the chemical reduction of Fe and Mn and their subsequent depletion from sediments. Manganese concentration in the clay-sized fraction was correlated significantly with Fe concentration ($r = 0.95$) in the six Dousman Ditch bottom sediment samples, indicating that the two elements were depleted simultaneously by chemical reduction.

Disproportionately high levels of Cd, Cr, Fe, Ni, Pb and Zn in the clay-sized fraction at the Dousman No. 1 site than at the other Dousman sites indicate that considerable portions of these metals were deposited in the neighborhood of the sewer outfall and showed little tendency to migrate. Metals that remain in suspension were transported through and exited the drainage ditch and did not accumulate in the intervening channel from Dousman site No. 2 to Dousman site No. 6. The high concentration of Cd, Pb, and Zn at Dousman No. 1 (3, 18 and 15 times greater than in "unpolluted" bottom sediments, respectively) were presumed to arise from storm water runoff of traffic-related pollutants in the Brookfield Shopping Center parking lot. Thus, a natural drainage ditch traversing through a bog was found to retain metal pollutants in the neighborhood of the outfall under low flow rates.

Metals in Suspended Sediments

Metal concentrations in suspended sediments were measured to determine the short-term sediment and associated pollutant input into a receiving body of water. Concentration of pollutants associated with the sediments are affected by many variables so that long-term trends are difficult to extrapolate from a small set of suspended sediment data. Metal concentrations in urban suspended sediment samples are affected by the length of the dry period preceding the storm event, the amount of dust and dirt accumulation on streets, street sweeping practices, the intensity of the storm event which influences the amount and particle size of dust and dirt removed from the surfaces, and the stage of the hydrograph when the samples are taken. Generally, the concentration of pollutants are highest during the first flush stage of the rising part of the hydrograph. Therefore, the concentrations of elements in each particle-size fraction of the suspended sediment samples (Tables 4 and 5) represented discrete samples for a specific event and for a particular portion of the hydrograph.

Two sets of suspended sediment samples (June 30 and July 18, 1977) were analyzed for concentration of elements in each particle-size fraction for a general comparison with the bottom sediments and soils. Unlike the bottom sediments, no general pattern or association of metal concentration with their sampling sites was observed for the suspended sediment samples. Differences in time of sampling relative to the hydrograph peak of a storm event was a source of wide variation in elemental composition of suspended sediments. Time of sample collection varied from 1 hr before peak flow to as much as 13 hr thereafter (Table 2). With the exception of samples affected by STPs and industrial discharges, the Al, Fe and Mn concentrations in the clay-sized

Table 6. Particle size distribution and element concentrations in each size fractions of Dousman Ditch bottom sediment

Sample*	Fraction	Particle size distribution,** %	Element, µg/g									
			Total P	Pb	Cd	Cu	Cr	Ni	Zn	Al	Fe	Mn
Dousman 1	Sand	20	314	141	0.68	7.9	7.4	4.3	39	2,890	7,190	261
	Silt	55	573	208	1.0	24	21	12	104	8,840	12,300	392
	Clay	25	2,220	932	5.0	31	102	62	671	41,800	54,800	574
Dousman 2	Sand	3	938	***	3.9	24	17	***	34	5,020	679	92
	Silt	42	1,170	36	2.0	14	15	23	45	10,300	7,960	138
	Clay	55	2,460	60	2.6	54	21	28	113	103,000	10,200	126
Dousman 3	Sand	7	652	55	0.91	5.8	9.8	13	42	6,200	6,650	378
	Silt	35	430	62	0.72	12	9.1	13	56	8,170	9,180	442
	Clay	58	1,190	163	1.5	44	59	36	200	40,600	29,500	361
Dousman 4	Sand	27	328	11	0.48	4.8	4.6	4	23	3,830	6,090	170
	Silt	32	971	46	0.37	17	11	13	54	5,900	14,700	220
	Clay	41	1,940	134	1.6	46	53	31	209	28,800	25,700	245
Dousman 5	Sand	22	294	10	0.14	4.6	4.7	3.4	37	3,070	6,520	202
	Silt	45	1,620	53	0.71	21	12	12	61	5,340	13,200	325
	Clay	33	2,090	124	1.7	38	41	27	184	23,400	23,800	344
Dousman 6	Sand	23	284	16	0.09	6.4	4.5	4.2	21	2,880	6,420	392
	Silt	40	501	38	0.34	12	9.5	9.0	37	4,890	10,900	289
	Clay	37	1,570	167	1.3	54	69	36	234	39,600	34,400	413
Pooled standard deviation+	Sand		152	6.1	0.20	0.80	1.5	2.3	7.2	1,050	1,370	27
	Silt		84	4.7	0.16	1.3	1.5	1.4	7.1	1,570	890	25
	Clay		153	25	0.27	3.1	5.6	5.9	22	11,470	1,025	10

*See Fig. 2 for location of sampling points along Dousman Ditch.
**Samples dispersed by ultrasonic treatment without prior removal of organic matter; clay size fraction is < 4 µm.
***No sample.
+Sp = $\sqrt{\text{Mean square error}}$.

fractions of the suspended sediments were found to be higher than in the clay-sized fractions of bottom sediments and lower than in the clay-sized fractions of the surface soils. Apparently, suspended sediments were less subject to leaching during aqueous transport than bottom sediments. High concentrations of Al, Fe and Mn in soils generally mask other possible sources of input for these metals in the suspended sediments. The few sediment samples that deviate from this trend and show high Al, Fe or Mn concentrations in their clay-sized fractions as compared to other sediment samples were suspected of receiving significant inputs of these metals from external sources. The concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the major soil types from the watershed were sufficiently low to permit the detection of additional input of these metals in the suspended sediment derived from surface soils.

The elemental composition of the clay-sized fraction of suspended sediment from the Donges Bay Road sampling site (Tables 4 and 5)--located in the upper reaches of the Little Menomonee River--was similar to the levels found in soils, and was considered to be "unpolluted" with these metals. The River Lane sampling site--located in the upper reaches of the Upper Menomonee River--was found to be polluted with Cd and Mn. This might be caused by inputs from the Germantown STP and/or an adjacent golf course. The settling pond at the Germantown STP selectively removes sediments that were able to deposit quickly and in so doing removed those sediments more likely to contribute to bottom sediment pollution; suspended sediments and associated pollutants from the STP were not removed at the settling pond. Another possibility was that the storm was of sufficient intensity to cause overflow and/or a more rapid flow of effluent which subsequently lowered the depositional capability of the STP settling pond. Pollutants generated in this fashion are more likely to be detected in suspended than in bottom sediments.

The Pilgrim Road suspended sediment sampling site was in the village of Menomonee Falls above the two Menomonee Falls treatment plants and drains 8739 ha of land, 78% of which is in agricultural and related land uses (9). It also receives storm water from the village of Menomonee Falls, which could explain the sharp increase in Pb arising from automobile traffic inputs. Lead concentration in the clay-sized fraction was significantly higher than the level in soil even though the sample was taken 12 hr after the peak of the hydrograph had been reached (Table 2). Although Zn is associated commonly with vehicular emission, no measurable increase over the soil level was observed. Possible explanations are 1. Zn is more soluble or more readily removed from streets during the initial phase of the storm than is P (12), 2. Pb in the sample arose from atmospheric fallout of automobile exhaust materials and contributes to pollutional loading for a longer time than Zn and 3. another unknown source of Pb exists which was not associated with Zn.

The next suspended sediment sampling site downstream from Pilgrim Road was 124th Street. It receives effluent from both treatment plants in the village of Menomonee Falls. Chromium, Cu, Ni, Pb and Zn in the clay-sized fraction of the suspended sediment were higher than the soil levels even when the smaple was taken 7 hr after the peak of the hydrograph (Table 2). This was in agreement with bottom sediment analysis of this portion of the Menomonee River--a large contribution of metals from the Menomonee Falls STP No. 1 outfall which was located after Pilgrim Road and before 124th Street. However, the Pb level at the 124th Street site was slightly lower than in the

Pilgrim Road site, even though the former was sampled closer to the time of peak flow (7 hr compared to 12 hr). The reduction of Pb concentration may be due to a lower density of streets near the 124th Street site than near the Pilgrim Road site. An effect due to dilution and deposition of Pb may occur as the river flows through the 4 kmn of agricultural land separating the two sites.

Although bottom sediments from the upper reaches of the watershed generally have lower metal concentrations in the clay-sized fractions than samples from the lower part of the Watershed, this was not always the case with suspended sediments. Suspended sediments from the next two sites below 124th Street--70th Street and Falk Corporation--had low Zn concentrations with values similar to those found at the Donges Bay Road and River Lane sites located in the upper part of the Watershed. These two samples were collected 12.5 hr following peak flow and dilution effects may have been significant during this part of the storm water runoff hydrograph.

Elemental composition of suspended sediments collected from the same sites for different storm events may show different trends resulting from differences in antecedent rainfall conditions and the stages of the hydrograph when the samples were collected. The suspended sediment sample collected at the Falk Corporation site on July 18, 1977 had lower Cd, Cr, and Pb concentrations in the clay-sized fraction than those found in the 70th Street sample; the opposite relationship was true for the June 30, 1977 sample. Flow rates during collection of the June 30 suspended sediment samples were higher than during collection of the July 18 suspended sediment samples (Table 2). The higher flow rate during the collection of the June 30 sample showed a correspondingly higher sand-sized fraction in the suspended sediments.

A suspended sediment sample from the Schoonmaker site--a highly urbanized medium density residential area--showed unusually high Al, Cd, Cu, Fe, Pb and Zn concentrations. One municipal sewage flow relief valve was located in this subwatershed but it was rarely in operation, and no industrial surface discharges existed (10). A combination of factors may explain these unusually high levels of pollutants 1. a low flow rate (1.98 cms peak) at Schoonmaker Creek and long contact time with pollutants, 2. a high degree of connected impervious areas (54%, ref. 16) and 3. a close enough proximity to the Industrial Valley of Milwaukee to receive atmospheric fallout from this source. Another medium density residential area--the Noyes Creek subwatershed--also showed an increase in Pb and Zn levels over the soil level but not nearly as high as the suspended sediment sample from Schoonmaker Creek. The Noyes Creek sampling site was located 8 km north of the Schoonmaker Creek site and was thus further away from the Industrial Valley of Milwaukee and also had a lower traffic volume.

Generally, the concentration of an element sorbed on the surfaces of clay-sized particles is higher than for silt-sized particles because the amount of element sorbed is proportional to the surface area per unit mass. In this investigation, this hypothesis was nearly always true with bottom sediments and soil samples (Tables 1, 4 and 5). However, pollutant sorption on silt-sized particles relative to clay-sized particles appeared higher for suspended sediments than for soils and bottom sediments. This may be due, in part, to the non-uniform distribution of silt-sized particles in the suspended sediment over the size range of 62 to 4 μm. The particle sizes were probably

skewed toward the 4 μm end of this range due to gravity settling of the coarser silt particles during transport (17). However, the skewed distribution of silt-sized particles cannot explain cases where the ratio is >1--i.e., where the element concentration in the silt-sized fraction is higher than in the clay-sized fraction. This was found for Cu and Zn in the Harbor samples and Ni in the Noyes Creek, Underwood Creek and Pilgrim Road samples. The high Ni concentrations in the silt-sized fractions may be due to the way in which metal abrades from metallic surfaces, resulting in metal chips that are not as finely divided as those which have passed through a vapor phase prior to sorption on solid surfaces. Dust and dirt remaining on impervious surfaces also may have been depleted selectively of its clay-sized fraction by wind and water erosion. During a storm, dust and dirt on impervious surfaces are washed into the river and become mixed with the suspended material from upstream. Thus, if the selective depletion of clay in urban street dust and dirt is an important factor for the enrichment of Ni in suspended sediments, then other elements should also show a concentration enrichment in the silt-sized particles. Aluminum, Pb and Zn concentrations in the silt-sized fraction of the suspended sediments were found to be higher than in the silt-sized fraction of bottom sediment or soil, but this enrichment was not as great as for Ni. The higher concentrations of certain elements in silt-sized fractions than in clay-sized fractions (without prior chemical or ultrasonic dispersion treatment in the fractionation procedure) also were observed for some suspended sediments (18) and on urban street dust and dirt samples (19).

Comparisons of elemental composition of suspended sediments from different locations and storm events were more difficult to make than for bottom sediments. Additional factors that must be included for a comparison of suspended sediments are the time of sampling relative to the peak of the hydrograph, antecedent rainfall conditions and street sweeping practices. The ratios of element concentrations in the silt-sized fractions to element concentrations in the clay-sized fractions were found to be generally higher in suspended sediment than in bottom sediment and soil. In some cases, metal concentrations in the silt-sized fractions were found to be greater than in the clay-sized fractions.

Excluding the anomalously high Pb content of the sample from Schoonmaker Creek, the average Pb and Cd concentrations for the June 30 and July 18, 1977 suspended sediment samples were 350 μg/g Pb and 1.9 μg/g Cd in clay-sized particles; 180 μg/g Pb and 0.48 μg/g Cd in silt-sized particles and 290 μg/g Pb and 1.4 μg/g Cd in the unfractionated sample. The average annual event loading of Pb and Cd from suspended sediment in the Menomonee River basin to Lake Michigan was calculated to be about 3000 kg/yr Pb and 15 kg/yr Cd with ~90% of the Pb in the clay-sized fraction. The calculation was based on a 3-yr average suspended solids loading of 10,455,000 kg/yr (11) and assuming the June 30 and July 18 suspended sediments were representative samples.

Metals in Urban Street Dust and Dirt

Urban street dust and dirt samples were dispersed and analyzed for their chemical composition in sand-, silt- and clay-sized fractions to provide an estimate of pollutant they contribute to storm water runoff. Concentrations of Al, Fe and Mn in the 91st Street and 13th Street dust and dirt samples were

lower than in the six mineral soils. However, Al, Fe and Mn concentrations in sand, silt and clay fractions of the 13th Street samples were lower than in the 91st Street samples for September 22 and 26, 1977. This relationship was consistent with surrounding land use. The 91st Street sampling site was located in the central portion of the Watershed, in a commercial-residential area nearer to agricultural land use areas. The Al, Fe and Mn concentrations in dust and dirt at 91st Street were closer to the values found for soils than was the case at 13th Street. The 13th Street sampling site was located near the Industrial Valley of Milwaukee and receives atmospheric fallout from it. An apparent higher Zn and lower Pb loading rate existed at 13th Street than at the 91st Street sampling site. Other metal concentrations in dust and dirt samples showed similar ranges at both sites (Tables 4 and 5).

Cadmium, Cr, Cu, Ni, Pb and Zn concentrations in sand, silt and clay fractions of urban street dust and dirt samples were found to be higher than the levels found in the respective fractions of the six mineral soils. Therefore, Cd, Cr, Cu, Ni, Pb and Zn input into the river is expected to increase as the source of sediment input shifts from agricultural soil to urban street dust and dirt. When comparing metal concentrations of urban street dust and dirt samples with bottom sediments, Cr and Ni concentrations in the clay-sized fraction of the bottom sediments sampled at the Nor-X-way B site and further downstream were as much as five times greater than the levels found in the dust and dirt samples. Thus, another other source of Cr and Ni was present, probably industrial sewage from the Menomonee Falls STP No. 1.

It was noted that Cr, Cu, and Ni concentrations in the coarser fractions of urban street dust and dirt samples were occasionally greater than the concentration in the finer-textured material--sand vs. silt and silt vs. clay. A similar situation was noted in the suspended sediment samples. Also the pooled standard deviations for Cu and Ni in the sand-sized fraction were greater than in the silt-sized or clay-sized fractions. These results indicate that a simple surface sorption model showing a higher concentration of sorbed element in the fine particle size fraction is insufficient to account for the concentrations of Cr, Cu and Ni in urban street dust and dirt samples. However, Cr, Cu and Ni originating as metallic chips or particles without passing through a vapor phase before being sorbed on to larger particles could explain the large pooled standard deviations of metal concentrations in the sand-sized fractions; and the high Cr, Cu and Ni concentrations in the coarser particles of urban street dust and dirt.

Other elements (Cd, P, Pb and Zn) were found to be less concentrated in the coarser fractions of urban street dust and dirt samples than in the fine fraction. The coefficients of variation for Cd, P, Pb and Zn in sand also were lower than for Cr, Cu and Ni in the sand fraction of the street dust and dirt samples. Much of the Cd, P, Pb and Zn from combustion of leaded gasoline and oil lubricants probably passes through a vapor phase prior to sorption on particle surfaces and tends to be concentrated on particles with largest surface area per unit mass. Thus, the surface sorption model was adequate to explain the distribution of Cd, P, Pb and Zn in the sand, silt and clay fractions of the urban street dust and dirt samples.

The efficiency of street sweeping for the removal of metals and P could be estimated by comparing total elemental composition of the urban street dust and dirt with the elemental composition of the fraction removed by street

sweepers. Table 7 lists the percentage of elements distributed in each particle size range. Thus, the elements can be divided into two main groups: those elements with a high distribution in the sand fraction (Cr, Cu, Fe, Mn, Ni and Zn), varying from 70 to 87%, and those elements with a lower distribution in the sand fraction (Al, Cd, P and Pb), varying from 41 to 58%. If street sweeping is efficient in removing all particles of the sand-sized fraction (>62 μm) but leaving behind silt- and clay-sized particles, then the removal of Cr, Cu, Fe, Mn and Ni would be more efficient than the removal of Al, Cd, P, and Pb--of which Cd, P and Pb were considered to be more hazardous to the environment (1). However, the distribution and removal efficiencies of elements should be viewed with caution. Two factors which work counter to each other were used in obtaining the distribution of elements in the particle sizes. The dust and dirt samples were collected in areas which were not swept. Therefore, the particle-size distribution of the samples is biased toward coarser-sized particles because coarse particles are less readily transported by wind and traffic movement. Antecedent rainfall conditions also affect particle-size distribution. This bias of particle-size distribution toward the coarser sizes was probably slight because of the frequency of rainstorms (Table 3). However, samples also were dispersed by ultrasound to ensure aggregate breakdown. Complete dispersion would lead to a greater proportion of the pollutants residing on fine particles. Ideally the elemental composition of the dust and dirt samples should be analyzed in two sets, i.e., with and without ultrasound dispersion prior to fractionation.

The Al, Fe and Mn concentrations in urban street dust and dirt samples were found to be lower than in the six mineral soils, while Cd, Cr, Cu, Ni, Pb and Zn were higher. Occasionally Cr, Cu and Ni concentrations in the coarse particle-size fractions of the dust and dirt samples were found to be greater than the concentration in the fine fraction. This was presumed to result from their presence in metal chips. Distribution of Cr, Cu, Ni, Fe and Mn was found to be associated to a greater extent with the sand fraction while Al, Cd, P, and Pb were associated with finer particles. A similar distribution pattern of elements in urban street dust and dirt particle size fractions with Cd, N, P, Pb and Zn in one group and Cr and Cu in another group was reported by Pitt (19).

Pollutional Classification of Sediments

Presently (January 1980) no national guidelines exist for identifying polluted bottom sediments or dredge spoils. However, Region V of the U.S. Environmental Protection Agency (U.S.-EPA) has developed interim guidelines for classifying Great Lakes harbor dredge spoils into three levels of contamination: non-polluted, moderately polluted and heavily polluted (Table 8, ref. 20). This classification scheme was based on statistical analysis of 260 dredge samples from 34 Great Lakes harbors which were analyzed for chemical composition of intact, unfractionated samples. Application of the guidelines was intended for dredge samples from harbors in this area and not for samples collected away from the harbor where particle-size distribution differs from that of harbor samples. However, a guideline for unfractionated samples cannot isolate the effect of particle-size distribution on elemental composition of the sediments. For example, suspended sediments are enriched

Table 7. Distribution of elements in each particle-size fraction of urban street dust and dirt samples

Parameter	Distribution, %		
	Sand	Silt	Clay
P	48(17.9)*	23(12.1)	28(6.2)
Pb	58(4.0)	18(5.2)	25(2.3)
Cd	41(6.6)	27(8.4)	31(8.3)
Zn	70(6.0)	13(2.5)	17(6.4)
Cu	81(6.8)	11(6.6)	8(1.5)
Al	52(20.7)	16(7.2)	32(15.3)
Fe	87(5.4)	8(4.2)	5(1.5)
Mn	78(5.1)	11(3.4)	11(2.1)
Cr	79(7.1)	10(4.8)	11(2.4)
Ni	82(5.2)	11(3.5)	7(2.4)

*Standard deviation in parentheses.

Table 8. Comparison of total elemental composition of soils, sediments and urban street dust and dirt with U.S.-EPA pollutional classification guideline for unfractionated dredge spoils

Sample/sampling location*	Element, µg/g								
	Total P	Pb	Cd	Zn	Cu	Cr	Ni	Fe	Mn
	U.S. EPA Dredge Guidelines for Pollution Levels of Unfractionated Sample								
Moderately polluted	420	40		90	25	25	20	17,000	300
Heavily polluted	650	60	6.0	200	50	75	50	25,000	500
	Soils								
Ozaukee sil (Ou)	690	16	0.24	42	27	26	16	16,800	916
Mequon sil (Mt)	998	17	0.30	34	31	27	22	27,000	757
Hochheim sil (Hm)	583	21	0.14	72	15	29	18	22,900	900
Ashkum sicl (As)	1,250	20	0.66	81	49	32	16	17,500	159
Pella sil (Ph)	760	21	0.41	96	20	42	14	24,900	645
Theresa sil (Th)	470	12	0.14	70	9	22	11	17,400	580
Houghton muck (Ht)	1,130	7	N.D.	65	34	19	25	27,500	311
	Bottom Sediment								
Little Menomonee River									
Dongee Bay Road (1)	521	9	0.26	53	11	11	9	12,600	220
County Q Road (2)	1,010	19	0.43	121	21	29	20	21,000	469
Road F near Road B (3)	410	17	0.39	105	11	11		11,000	522
Appleton Avenue (4)	307	31	0.35	107	17	14	17	11,800	678
Upper Menomonee River									
Friestad (5)	687	11	0.42	62	18	16	14	21,600	241
River Lane (6)	414	14	0.16	43	9.8	10	8	9,300	303
Maple Road (7)	333	15	0.25	46	12	12	10	13,400	256
Menomonee Falls (8)	995	32	0.32	106	19	27	19	18,400	515
Nor-X-way A*** (10)	465	82	0.50	286	27	17	13	10,700	365
Nor-X-way B*** (11)	1,060	112	0.64	243	29	56	**	12,400	444
Lily Creek (12)	2,470	181	1.0	466	55	100	97	22,500	401
Dretzka Creek (13)	2,720	174	1.3	475	63	98	**	26,000	776
124th Street (14)	2,030	94	0.74	271	40	51	97	23,900	485
Lower Menomonee River									
Capitol Drive (15)	609	54	0.68	98	35	45	**	13,700	820
70th Street (16)	235	45	0.29	90	14	11	8	6,700	240
Falk Corporation (17)	1,100	487	9.0	647	219	187	55	22,900	570
Harbor (18)	370	440	1.4	193	69	58	13	10,900	287
Dousman Ditch									
Dousman 1	933	376	1.9	233	23	39	23	21,900	411
Dousman 2	1,870	48	2.4	82	36	18	25	8,970	130
Dousman 3	855	117	1.2	135	29	37	26	20,300	396
Dousman 4	1,190	73	0.9	109	26	26	18	16,900	217
Dousman 5	1,480	67	0.9	96	23	20	15	15,200	304
Dousman 6	847	81	0.6	106	26	30	18	18,600	359

Table 8. Continued

Sample/sampling location*	Element, µg/g								
	Total P	Pb	Cd	Zn	Cu	Cr	Ni	Fe	Mn
				Suspended Sediment+					
Upper Menomonee River									
River Lane (673001)	3,500	68	1.9	440	35	37	28	66,000	1,400
Pilgrim Road (683002)	1,900	207	N.D.	352	45	55	66	38,000	987
124th Street (683001)	1,790	163	0.6	356	56	117	67	36,800	700
Little Menomonee River									
Donges Bay Road (463001)	1,700	39	0.3	285	44	56	45	46,400	730
Noyes Creek (413011)	1,060	164	0.5	478	41	49	61	37,900	582
Appleton Avenue (413008)	950	57	0.3	292	33	42	50	31,300	594
Lower Menomonee River									
Underwood Creek (413007)	1,260	485	1.4	570	71	70	58	44,800	710
Honey Creek (413006)++	1,180	570	1.4	420	62	45	38	35,100	573
Honey Creek (413006)	1,540	298	1.3	544	69	99	50	36,900	534
70th Street (413005)++	1,260	437	2.0	500	82	103	62	36,480	646
70th Street (413005)	1,270	158	0.7	268	66	90	48	34,500	574
Schoonmaker Creek (413010)	1,800	1,360	3.2	3,180	89	79	56	162,000	831
Falk Corporation (413004)++	1,440	668	3.9	856	125	106	41	51,000	1,080
Falk Corporation (413004)	1,100	115	0.7	280	63	52	47	23,200	530
Harbor	2,520	616	3.4	1,560	398	199	142	89,700	1,410
				Urban Street Dust and Dirt					
13th Street Bridge, 9/22/77	134	214	2.4	548	172	37	41	44,800	305
13th Street Bridge, 9/26/77	138	362	3.6	626	281	44	66	62,000	370
91st Street, 9/22/77	190	769	3.0	737	282	53	53	68,000	504
91st Street, 9/26/77	140	1,227	5.5	1,000	277	32	70	59,500	624

*Numbers or letters in parentheses correspond to sampling sites shown in Fig. 1; for Dousman Ditch sample locations see Fig. 2.
**No sample.
***A-before confluence; B-after confluence.
+Samples were collected on July 18, 1977 except where noted.
++Samples were collected on June 30, 1977.
N.D. Not detected.

with clay as compared to bottom sediment samples due to selective deposition of coarse particles. Bottom sediments collected from segments of the river where water flow rate is lower tend to have higher amounts of clay-sized particles than at sites where flow rate is higher. An enrichment in the content of clay-sized particles increases the concentration of surface sorbed elements in unfractionated samples. This apparent increase in element concentration of unfractionated samples can be isolated by fractionation of samples prior to determination of their composition.

The Region V of U.S.-EPA dredge spoil guidelines showed greater tolerance for polluted samples when the guidelines were applied to the harbor bottom sediment samples collected in this study. Chromium and Zn in the harbor bottom sediments were classified as moderately polluted according to the Region V of EPA scheme but had the highest and second highest concentration of these metals in the clay-sized fraction.

In general, unfractionated suspended sediment samples had higher total concentrations of surface-sorbed elements than unfractionated bottom sediments or surface soils (Table 8). However, many suspended sediment samples if they were classified on the basis of elemental composition in the clay-sized fraction.

A more important advantage in analyzing fractionated rather than intact samples can be seen in the greater precision of locating areas that received high pollutant inputs, even though the river tends to disperse pollutants from upstream and carry them downstream. For example, the gradual decline in elemental composition in the clay-sized fraction of bottom sediments from Nor-X-way B to Dretzka Creek and the slight increase at Capitol Drive (Tables 4 and 5) would not be detected using unfractionated samples (Table 8). The relationship of elemental composition in Lily Creek compared to Nor-X-way B unfractionated bottom sediment samples was the reverse of the relationship in the clay-sized fraction.

It is recommended that the pollutional guidelines for bottom sediment be based on elemental composition of the clay-sized fraction of unpolluted bottom sediments or major soils in the watershed which potentially erode and contribute to the sediment loading. Comparisons of soil composition with sediment composition should take into account the greater leaching that sediments are subject to and the differences in pH and Eh between soils and sediments.

It was noted that the elemental composition of the clay-sized fractions of "unpolluted" bottom sediments were lower than soils except for Cd, Pb, and Zn. It was suspected that all bottom sediment samples received C, Pb and Zn inputs from atmospheric fallout in sufficient amounts to balance off losses due to leaching, Eh and/or pH changes. Each of these metals is associated with vehicular emission.

Dispersibility of Soils

Sediment is the major water pollutant. Soils with the greatest potential to be dislodged by rain impaction tend to contribute more sediments to the

storm water runoff. The finer-textured materials that are dispersed stay in suspension longer than coarse-textured materials and are transported a greater distance overland. Once transported into the waterways the finer-textured materials tend to be the carriers of pollutants. However, clay particles form aggregates and the aggregates deposit quicker than the dispersed particles of which they are comprised. Consequently, nutrients and pollutants sorbed by aggregates are less available to the biota. The dispersibility of soils may be an indirect method of evaluating the availability of nutrients and polluants sorbed on the surface as well as the potential of the soil to erode.

Six surface mineral soils, one organic soil, and two subsurface soils were shaken with water to simulate their dispersion and transport in an aquatic system. Their particle-size distribution was determined (Table 9). The ratio of the particle size distribution by shaking and by ultrasonic treatment provided a number which measures the ease of dispersibility of a particular soil (Table 10). This number could serve as a ranking factor for nutrient or pollutant availability to the lake biota and for the potential of the soil to erode.

A significant negative linear correlation between the dispersion ratio of the clay-sized fraction and the organic C content of six surface mineral soils existed for short periods of shaking: P = 5% for 16 hr and P = 1% for 4 hr shaking (Table 11). Organic matter facilitates aggregation of soil particles (21). As the length of the agitation period increased (32 to 128 hr), the binding properties of organic matter were reduced and the linear correlation was less significant. It was thought that the six surface mineral soils were too homogeneous and represented a narrow range of soil organic carbon (1.2 to 5.7% C, Table 11). Therefore, two subsurface soils with lower organic carbon content ($\sim$0.5%) and one organic soil (44% organic C) were included in the dispersibility study. The significance levels of the linear correlations remained unchanged when the two subsurface soils were included in the analysis for the 4- and 16-hr dispersion treatments. Linear correlation between organic C and dispersion ratio became insignificant when the organic soil also was included in the analysis.

The correlation between dispersibility and organic carbon content also was analyzed for "log x" and "1/x" relationships. In both cases the level of significance was high for the 1-, 4- and 16-hr shaking treatments. When two subsurface soils were included in the analysis between organic C and clay-sized particle dispersion ratio, it was noted that the "1/x" relationship was consistently better correlated than "log x;" which was consistently better correlated than "x" (linear) for dispersion treatments of 0.5 to 64 hr. Similarly, when the organic soils as well as the two subsurface soils were included in the correlation analysis, the "1/x" relationship was consistently better correlated than "log x", which was better than "x" for 4 to 64 hr dispersion treatments. Thus "1/x" and "log x" relationships between clay-sized particle dispersion ratio and organic C content of soil were more applicable to a wider diversity of soils than the linear relationship. The "1/x" relationship predicts that increasing organic C content of soil--e.g., with the addition of sewage sludge--would benefit the aggregate stability of soils with low organic C more than soils with high organic C.

A low correlation between soil erodibility and organic C content of soils with >4% organic C was noted by Wischmeier et al. (22). The preceding results

Table 9. Dispersability, by shaking, of soils in the Menomonee River Watershed

Time of shaking, hr	Particle-size fraction	Amount of fraction dispersed, %								
		Ozaukee sil	Ozaukee subsoil	Mequon sil	Mequon subsoil	Hochheim sil	Ashkum sicl	Pella sil	Theresa sil	Houghton muck
0.5	Sand	61.7	65.7	77.0	73.4	70.6	64.8	61.9	53.3	
	Silt	37.0	29.3	22.2	24.1	27.6	33.5	35.7	45.3	
	Clay	1.2	4.9	0.8	2.5	1.8	1.7	2.3	1.4	
1	Sand	51.8	60.4	63.3	69.0	56.8	45.2	51.4	37.7	
	Silt	46.3	32.1	35.3	27.3	41.2	52.4	45.6	60.2	
	Clay	1.9	7.4	1.4	3.6	2.0	2.4	3.0	2.1	
4	Sand	48.4	57.0	64.6	68.0	55.5	52.7	50.6	43.0	86.1
	Silt	48.0	31.6	32.3	26.5	40.3	43.3	44.6	54.0	11.9
	Clay	3.6	11.5	3.0	5.6	4.2	4.0	4.8	3.0	2.0
16	Sand	37.6	50.5	58.5	64.8	46.6	45.6	42.3	34.3	81.8
	Silt	57.4	30.2	37.0	25.4	46.8	47.9	50.7	61.6	15.0
	Clay	5.0	19.3	4.4	9.7	6.6	6.4	7.0	4.1	3.2
32	Sand	41.7	49.2	49.8	66.5	46.0	45.2	32.7	35.3	64.6
	Silt	52.2	29.5	42.3	23.0	45.8	46.5	58.6	60.2	29.1
	Clay	6.1	21.3	7.9	10.5	8.2	8.3	8.7	4.6	6.3
64	Sand	39.8	45.4	54.1	67.6	44.8	39.5	32.9	35.6	66.8
	Silt	52.5	27.6	34.5	19.4	44.4	50.2	56.7	58.2	24.4
	Clay	7.7	27.0	11.4	13.0	10.8	10.2	10.4	6.1	8.8
128	Sand	38.8	43.7	49.4	66.1	36.5	36.1	32.7	30.4	58.0
	Silt	54.1	29.7	38.5	21.5	50.5	51.5	57.7	62.7	28.3
	Clay	7.1	26.6	12.0	12.4	13.0	12.4	9.6	6.9	13.6

Blanks indicate no data.

Table 10. Dispersion ratio of the clay-sized fraction (shaking/ultrasonic)

Time of shaking, hr	Soils*								
	Ozaukee sil	Ozaukee subsoil	Mequon sil	Mequon subsoil	Hochheim sil	Ashkum sicl	Pella sil	Theresa sil	Houghton muck
0.5	0.06	0.15	0.03	0.15	0.07	0.05	0.06	0.08	
1	0.10	0.22	0.05	0.21	0.07	0.07	0.08	0.13	
4	0.19	0.35	0.10	0.33	0.16	0.11	0.13	0.19	0.03
16	0.26	0.59	0.15	0.57	0.24	0.18	0.19	0.26	0.05
32	0.32	0.65	0.27	0.62	0.30	0.24	0.24	0.29	0.10
64	0.40	0.82	0.39	0.76	0.40	0.29	0.28	0.38	0.15
128	0.37	0.81	0.41	0.73	0.48	0.35	0.33	0.43	0.22

*Organic carbon contents of soils are: Ozaukee sil - 1.8%, Ozaukee subsoil - 0.50%, Mequon sil - 4.5%, Mequon subsoil - 0.49%, Hochheim - 2.5%, Ashkum sicl - 5.7%, Pella sil - 3.4%, Theresa sil - 1.2% and Houghton muck - 44.2%.
Blanks indicate no data.

Table 11. Linear, inverse and log correlation coefficient between soil organic carbon content and clay-sized fraction dispersion ratio

Time of shaking, hr	6 Suface soils			6 Surface soils + 2 subsoils			6 Surface soils + 2 subsoils + 1 organic soil		
	x	1/x	$\log_{10}$ x	x	1/x	$\log_{10}$ x	x	1/x	$\log_{10}$ x
0.5	-0.762*	0.790*	-0.797*	-0.804**	0.981**	-0.940**			
1	-0.775*	0.928**	-0.874**	-0.822**	0.987**	-0.959**			
4	-0.935**	0.904**	-0.951**	-0.859**	0.985**	-0.970**	-0.612	0.968**	-0.930**
16	-0.883**	0.853*	-0.898**	-0.789**	0.989**	-0.932**	-0.547	0.967**	-0.879**
32	-0.763*	0.642	-0.730*	-0.740*	0.976**	-0.902**	-0.569	0.967**	-0.879**
64	-0.580	0.492	-0.553	-0.736*	0.963**	-0.892**	-0.555	0.953**	-0.867**

*Significant at P = 0.05.
**Significant at P = 0.01.
Blanks indicate no data.

may provide an improvement to the Wischmeier et al. equation (23 and 24) for predicting soil erodibility. The equation assumed a negative linear relationship between soil erodibility and organic C content in the range of 0.9 to 4% organic C. The present findings also showed a significant linear correlation in this range for 4 to 16 hr shaking treatments. However, when soils with a wider range of organic C (0.5 to 44% C) were included, a "1/x" relationship provided better correlation than the linear relationship.

From the above results, it is clear that soils eroding to waterways do not disperse completely during the early stage of transport. For example, after 4 hr of shaking 19% of the clay in the Ozaukee soil was dispersed into clay-sized particles while the remaining 81% of the clay remained intact as silt-sized or larger aggregates (calculated from Table 10). Settling ponds that capture silt-sized or larger particles and aggregates while allowing clay-sized particles to pass through are able to capture 80 to 90% of the clays for the six mineral surface soils for conditions simulated by a 4 hr shaking period. In certain parts of the upper reaches of the Menomonee River, e.g., behind dams (Menomonee Falls Dam and Lily Creek) and widening areas in the river (Dretzka Creek and 124th Street), high contents of clay-sized particles (33 to 58%) were found in bottom sediments. For sediments deposited in the Milwaukee Harbor there is a longer transport distance for eroded materials from the upper part of the watershed and a correspondingly greater dispersion of aggregates during transport. Dispersed clay-sized particles will remain in suspension and exit the harbor area; hence, the clay-sized fraction of the Milwaukee Harbor bottom sediments are quite low (2 to 14%, ref. 8).

One of the methodological problems with the procedure for estimating soil erodibility is soil preparation. Soil samples were forced-air dried and ground to pass a 10-mesh sieve prior to analysis. Such treatment undoubtedly affects the soil aggregates. However, without some drying and sieving, samples would be less uniform, and the reproducibility of the results would be diminished. The organic soil and subsurface soils were not forced-air dried to avoid conversion of the materials into hydrophobic aggregates, although they were sieved prior to the dispersion treatment. The end-over-end shaking treatments to simulate transport of soil in an aqueous medium was not fully investigated, i.e., the optimum soil:water ratio and rotation speed were not evaluated. A 1:10 w:v soil:water ratio as well as the shorter time period (1 to 16 hr) may approximate the onset of erosion conditions but not for long term transport to deposition and resuspension of bottom sediments in the river.

Extractability of Metals and Phosphorus

During aqueous transport of soils and sediments, metals and P may be desorbed from surfaces. The amount of element that could be desorbed rapidly (in minutes to a few hours) into the aqueous phase was estimated by analyzing the supernate obtained from end-over-end and ultrasound dispersion procedures. The amount of metals and P exracted from the solid surface during the laboratory dispersion and fractionation procedures was also a measurement of the error in determining element concentrations in solids caused by desorption. Those elements with the greatest tendency to be desorbed from surfaces would show the greatest error. This may have an effect on the biological availability of specific elements. Thus, the supernates from the

dispersion treatments (end-over-end shaking and ultrasound) were collected and analyzed (Table 12).

Supernate samples from the shaking treatment of the six mineral soils for 1 to 16 hr were digested without prior filtration; while supernate samples from the 32 to 128 hr shaking treatment were passed through a 0.4 μm polycarbonate membrane filter using an all plastic (polycarbonate) filter appratus. Element concentrations (normalized to 1 g of solids) in the unfiltered supernate following 1 to 16 hr shaking treatments were found not to be significantly different from each other for the different shaking periods as shown by the pooled standard deviations of the individual means (Table 12). Thus, the mean amounts of elements removed from the solids by 1 to 16 hr shaking treatments for each of the six soils were computed and designated as the "unfiltered shaking treatment group" (Table 12). Similarly, the mean value of elements removed from the solids by 32 to 128 hr shaking treatments for each of the six soils were computed and designated as the "filtered shaking treatment group" (Table 12). The amount of Fe was found to be higher in the supernates of the "unfiltered group" than in the "filtered group." This was attributed to the presence of microcrystalline and amorphous Fe oxides of low specific gravity that were not removed from the supernate by centrifugation but were removed by filtration. The removal of microcrystalline and amorphous Fe oxide by filtration did not significantly reduce the amount of Al, Cu, Mn and P found in the supernate even though some elements may have been sorbed by the Fe oxides. The amount of Zn extracted apparently increased with dispersion time, i.e., a greater dissolution of Zn in the "filtered" than "unfiltered" samples.

The amount of element extracted per gram of sample for "filtered" and "unfiltered" supernate samples of ultrasound treated soils were determined (Table 12). Ultrasound treatment of soils represents an extreme erosive condition as compared to end-over-end shaking. The amount of Fe extracted by the supernate per gram of sample was greater for ultrasound-treated than for shaken soils; and greater for "unfiltered" than for "filtered" samples.

The relative amount of element extracted from the solids during dispersion and fractionation was calculated by taking the ratio of the total element in the supernate to the total element in the solids (sand-, silt- and clay-sized particles). This ratio was computed from values in Tables 1, 8 and 12. The ratio of element loss from each of the six mineral soils were pooled together to obtain a mean value and standard deviation for each element (Table 13). Ratios of element loss from bottom sediments were determined similarly (Table 13). This was done on the assumption that the amount of element released into the supernate was proportional to the amount present at the solid surfaces. Thus, the ratio would remain relatively constant even though the total amount of a given element extracted and the amount present in the solid phase varied for different samples. The amount of element removed from the solid phase into the supernate during ultrasound fractionation of soils varied from 1 to 8%; and from 0.3 to 2% from bottom sediments (Table 13). Lower ratios of element loss from bottom sediments were probably caused by prior release of the more soluble components during their transport in the river.

If a sequence of increasing extractability were constructed from the "filtered supernates" of soils receiving a shaking treatment (Table 13) the

Table 12. Elements extractable from soils by end over end shaking and ultrasonic treatment

Treatment	Sample	Element, µg/g								
		Total P	Pb*	Cd*	Cu	Cr*	Ni*	Zn	Al	Fe	Mn
Shaking, unfiltered	Ozaukee silt loam	21.6			0.15			0.22	29	19	0.44
	Mequon silt loam	31			0.22			0.25	24	17	0.41
	Hochheim silt loam	3.2			0.27			0.24	37	27	0.67
	Ashkum silty clay loam	37			0.12			0.24	27	13	0.20
	Pella silt loam	4.5			0.36			0.15	10	12	0.26
	Theresa silt loam	10.7			0.07			0.19	29	18	0.47
	Pooled std. dev.	2.97			0.042			0.09	11.8	5.5	0.10
Shaking, filtered	Ozaukee silt loam	19	0.079	0.005	0.22	0.022	0.011	4.19	36	3.3	0.42
	Mequon silt loam	26	0.078	0.013	0.33	0.031	0.040	1.25	69	9.1	4.06
	Hochheim silt loam	3.0	0.022	0.007	0.13	0.017	0.022	0.49	57	6.3	1.04
	Ashkum silty clay loam	40	0.010	0.006	0.35	0.032	0.034	0.64	53	2.2	0.31
	Pella silt loam	2.8	0.035	0.009	0.15	0.026	0.023	3.31	89	4.0	0.20
	Theresa silt loam	8.1	0.027	0.002	0.11	0.028	0.037	1.94	33	2.7	0.27
	Pooled std. dev.	6.7	0.044	0.003	0.062	0.017	0.017	0.86	12	5.0	1.6
Ultrasonic, unfiltered**	Ozaukee silt loam	53			1.4	0.67	0.64	2.05	604	487	29
	Mequon silt loam	42			0.67	0.24	0.60	0.62	119	127	16
	Hochheim silt loam	15	0.67	0.02	0.25	0.24	0.12	0.59	228	164	12
	Ashkum silty clay loam	75		0.03	0.79	0.32	0.07	0.57	178	152	1.6
	Pella silt loam	16		0.02	0.48	0.44	0.17	0.58	156	161	2.9
	Theresa silt loam	52	0.85	0.02	0.66	1.34	0.36	2.35	1,270	931	33
Ultrasonic, filtered**	Ozaukee silt loam	57	0.097	0.020	1.07	0.57	0.22	2.2		71	12
	Mequon silt loam	63	0.017	0.015	1.00	0.33	0.14	1.1		35	3.1
	Hochheim silt loam	19	0.040	0.016	0.33	0.45	0.15	1.0		31	4.7
	Askhum silty clay loam	42	0.005	0.011	0.67	0.12	0.07	0.67		32	0.25
	Pella silt loam	31	0.077	0.020	0.33	0.23	0.06	0.47		24	0.40
	Theresa silt loam	26	0.047	0.017	0.27	0.40	0.17	0.93		37	5.3

*Analyzed by graphite furnace AAS.
**Samples not replicated hence no pooled standard deviation for individual means.
Blanks indicate that concentrations are below detection limit.

Table 13. Extractability (%) of elements contained in soils and bottom sediments as affected by different dispersion techniques

Element	Dispersion technique			
	Shaking		Ultrasonic	
	Unfiltered	Filtered	Unfiltered	Filtered
		Soils		
P	2.0 ± 1.2(6)*	1.9 ± 1.2(6)	5.5 ± 3.2(6)	5.0 ± 1.9(6)
Pb		0.2 ± 0.18(6)	4.9 ± 2.4(2)	0.3 ± 0.2(6)
Cd		2.6 ± 1.5(6)	7.8 ± 5.2(4)	7.1 ± 4.0(6)
Cu	0.9 ± 0.6(6)	0.9 ± 0.2(6)	3.3 ± 2.2(6)	2.4 ± 1.0(6)
Cr		0.1 ± 0.03(6)	2.0 ± 2.0(6)	1.3 ± 0.7(6)
Ni		0.2 ± 0.1(6)	1.9 ± 1.4(6)	0.8 ± 0.4(6)
Zn	0.4 ± 0.2(6)	1.8 ± 1.4(6)	2.0 ± 1.7(6)	2.0 ± 1.8(6)
Al	0.1 ± 0.06(6)	0.3 ± 0.07(6)	1.3 ± 1.2(6)	
Fe	0.08 ± 0.03(6)	0.02 ± 0.01(6)	1.8 ± 1.9(6)	0.2 ± 0.01(6)
Mn	0.04 ± 0.05(6)	0.2 ± 0.2(6)	2.3 ± 2.0(6)	0.6 ± 0.5(6)
		Bottom sediment		
Pb		0.06 ± 0.07(4)	1.5 ± 1.8(13)	
Cd		0.7 ± 0.1(4)	2.0 ± 1.0(10)	
Cu			1.0 ± 5.0(14)	
Cr		0.04 ± 0.02(4)	0.5 ± 0.4(13)	
Ni			1.6 ± 1.0(10)	
Zn		0.3 ± 0.01(4)	1.0 ± 1.0(15)	
Al			0.4 ± 0.3(14)	
Fe		0.03 ± 0.03(4)	0.3 ± 0.3(15)	
Mn		0.3 ± 0.2(4)	0.5 ± 0.3(15)	

*Figure in parenthesis corresponds to number of samples.

order would be Fe < Cr = Mn = Ni = Pb $\leq$ Al $\leq$ Cu < Zn $\leq$ P $\leq$ Cd (Table 14). With the exception of Ni, this sequence resembles the decreasing order of sorption of divalent metal ions on to Fe gel which is Pb > Cu > Zn > Ni > Cd (25). The sequence of increasing order of extractability also corresponds closely with the increasing order of first hydrolysis constants of metals with the exception of Ni; Fe(III) < Cr(III) < Al < Cu(II) < Ni(II) < Zn < Cd (26). Extractability ratios of "unfiltered supernates" from soils receiving a shaking treatment show a similar trend to the "filtered supernates"--Mn, Fe and Al in the less extractable group and Zn, Cu and Pb in the more extractable group. An increasing order of extractibility also was constructed for ultrasound treated soils and bottom sediments (Table 14). Although the mean values of the extractability ratios were lower for bottom sediment supernates than for soil supernates after ultrasound treatment, only Fe and Mn ratios of bottom sediments were significantly different from soils (90% confidence level using Student's T test). Reducing conditions in the bottom sediments augment the dissolution of Mn and Fe. It is important to note however, that the dissolution and desorption of elements from bottom sediments is not complete. If bottom sediments were resuspended, further release of elements to the overlying water would occur with Cd and P being the most extractable. This is of particular interest because Cd and P are considered to be very important pollutants by the U.S.-Canada IJC (1). Although the concentration of Cd was low in soil and sediments, it consistently had the highest extractability ratio for soil and bottom sediments with either ultrasound or end-over-end shaking dispersion. Thus, a higher proportion of total Cd and P in the solids can be extracted by water in a relatively short period of time (minutes to a few hours) as compared to other elements.

Correlation Analysis

Concentrations of elements in soil, bottom and suspended sediments and their supernatant liquids may be correlated together due to a common origin or association with a common source. To determine this, correlation coefficients and plots were obtained for pairs of different elements in each particle-size fraction of soils, bottom and suspended sediments and supernates; and the amounts of elements recovered in the supernate were compared with their concentrations in the solid phase of the soils and bottom and suspended sediments. High correlation coefficients were considered significant if the plots of data points were not controlled by a few points.

Six soils were considered to be too small a sample for making generalizations about soil properties, however, they were useful as references and for comparisons with bottom and suspended sediments. No significant correlations existed between different elements in the sand-, and silt-sized fractions of bottom and suspended sediments. Cadmium, Pb and Zn (Fig. 3) and Cr, Cu and Ni were correlated significantly with each other in the clay-sized fractions of the bottom sediments. Cadmium, Pb and Zn in the clay-sized fractions of suspended sediments also were correlated with each other (Fig. 3). These correlations were not found in soils which suggests that soils were not the primary sources of these metals, and vehicular emission and/or industrial effluent contributed to their presence in the clay-sized fractions of the sediments. The area surrounding several sediment sampling sites had fairly high density automobile traffic: near well-traveled roads (Road F near B and Nor-X-way A); parking lots (Dousman Ditch); urban areas with a higher degree of impervious areas (Noyes Creek and Schoonmaker Creek); an area with

Table 14. Increasing order of extractability of various elements using different dispersion techniques

Dispersion technique	Order of extractability
	Soils
Shaking, unfiltered	Mn < Fe < Al < Zn < Cu < P
filtered	Fe < Cr = Mn = Ni ≤ Pb ≤ Al ≤ Cu < Zn < P < Cd
Ultrasonic, unfiltered	Al ≤ Fe = Ni = Cr = Zn = Mn < Cu < Pb < P < Cd
filtered	Fe = Pb ≤ Mn ≤ Ni < Cr < Zn ≤ Cu < P < Cd
	Bottom sediment
Shaking, filtered	Fe ≤ Cr ≤ Pb < Mn = Zn < Cd
Ultrasonic, unfiltered	Fe ≤ Al ≤ Mn = Cr < Cu = Zn ≤ Pb ≤ Ni ≤ Cd

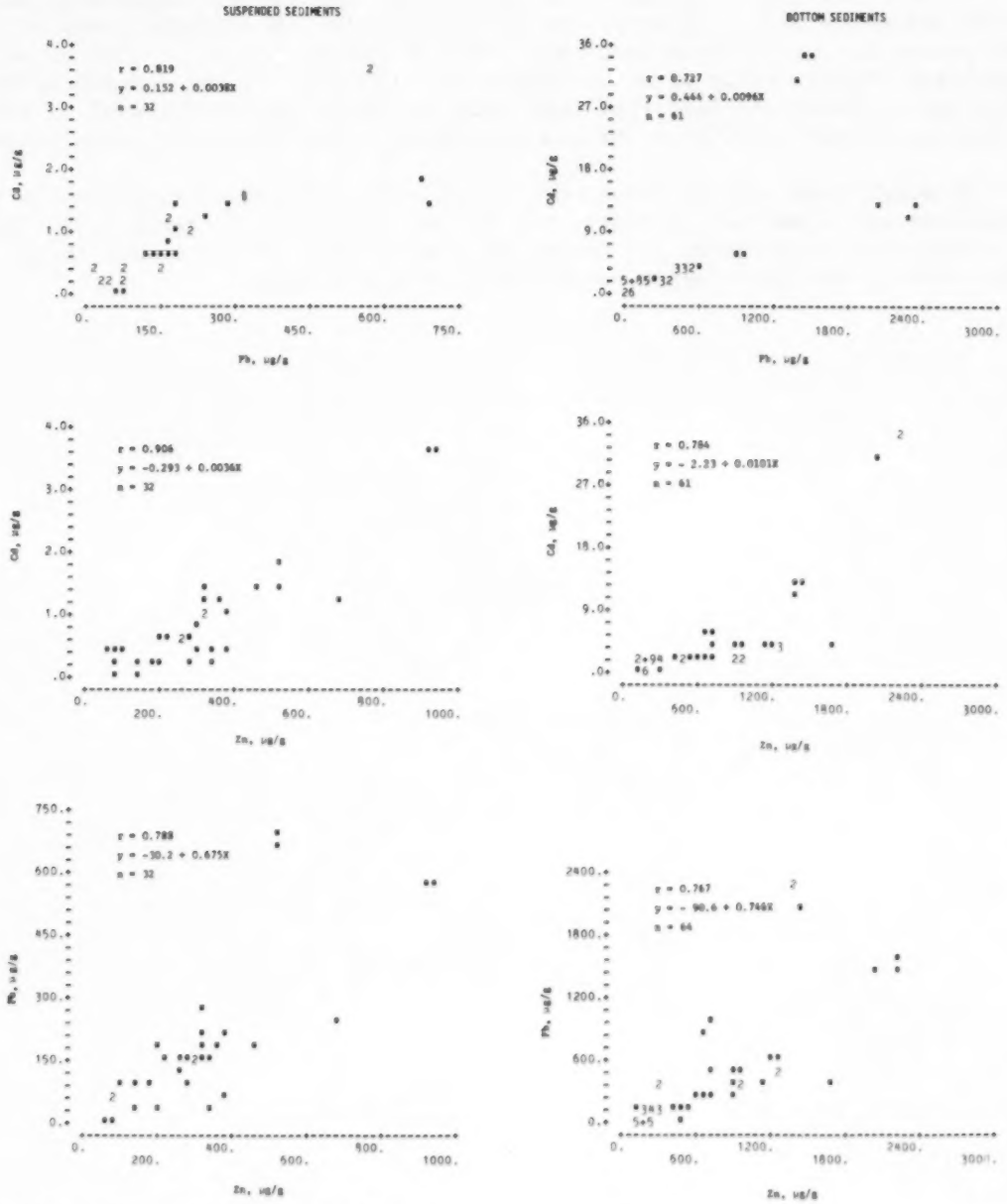

Fig. 3. Simple correlations between concentrations of lead and cadmium, zinc and cadmium and zinc and lead for the clay fractions of suspended and bottom sediments of the Penobscot River.

large amounts of connected impervious surfaces in its immediate surrounding (Pilgrim Road), indicating that vehicular emission was probably the major source of these metals in the sediment samples.

All element concentrations from ultrasound "unfiltered" supernates of bottom sediments and soils also were pooled together as a single group of 37 data points for correlation analysis. Only Al and Fe in the supernates were correlated significantly with each other ($r = 0.895$). It was concluded that soils and sediments derived from soil were the major contributors of Al and Fe to the supernatant solutions which accounts for their degree of correlation.

No significant correlations were found between elements extracted in the supernates and elemental concentration in the clay-sized fraction. The lack of correlation is probably due to the diverse sources of pollutants in an urban setting and the diverse solubilities of the elements.

REFERENCES

1. Pollution from Land Use Activities Reference Group. Environmental Management Strategy for the Great Lakes Systems. International Joint Commission, Windsor, Ontario, 1978.

2. Southeastern Wisconsin Regional Planning Commission. A Comprehensive Plan for the Menomonee River Watershed. Vol. I: Inventory Findings and Forecasts. Waukesha, Wisconsin, October 1976. p. 71.

3. Southeastern Wisconsin Regional Planning Commission. A Comprehensive Plan for the Menomonee River Watershed. Vol. 1: Inventory Findings and Forecasts. Waukesha, Wisconsin, October 1976. p. 157.

4. Genrich, D. A. and J. M. Bremner. A Re-evaluation of the Ultrasonic Vibration Method of Dispersing Soils. Soil Sci. Soc. Amer. Proc. 36:944-947, 1972.

5. U.S. Environmental Protection Agency. Manual of Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency Report No. EPA-625/6-74-003. Environmental Research Center, Cincinnati, Ohio, 1976.

6. Ediger, R. D. Atomic Absorption Analysis with the Graphic Furnace Using Matrix Modifications. Atomic Absorption Newsletter 14:127-130, 1975.

7. Tabatabai, M. A. and J. M. Bremner. Use of the Leco Automatic 70 Second Carbon Analyzer for Total Carbon Analysis in Soils. Soil Sci. Soc. Amer. Proc. 34:608-610, 1970.

8. Bannerman, R., J. G. Konrad and D. Becker. Effects of Tributary Inputs on Lake Michigan during High Flows. Final Report of the Menomonee River Pilot Watershed Study, Vol. 10, U.S. Environmental Protection Agency, 1979.

9. Simsiman, G. V., J. Goodrich-Mahoney, G. Chesters and R. Bannerman. Land Use, Population and Physical Characteristics of the Menomonee River Watershed. Part III: Description of the Watershed. Final Report of the Menomonee River Pilot Watershed Study, Vol. 2, U.S. Environmental Protection Agency, 1979.

10. Southeastern Wisconsin Regional Planning Commission. A Comprehensive Plan for the Menomonee River Watershed. Vol. I: Inventory Findings and Forecasts. Waukesha, Wisconsin, October 1976. pp. 236-247.

11. Bannerman, R. B., J. G. Konrad, D. Becker and G. V. Simsiman. Surface Water Monitoring Data. Part I: Quality of Runoff from Mixed Land Uses. Final Report of the Menomonee River Pilot Watershed Study, Vol. 3, U.S. Environmental Protection Agency, 1979.

12. Shaheen, D. G. Contribution of Urban Roadway Usage to Water Pollution. U.S. Environmental Protection Agency EPA-600/75-004, 1975.

13. Sylvester, R. O. and F. B. Dewalle. Character and Significance of Highway Runoff Waters: A Preliminary Appraisal. Dept. of Civil Engineering, Univ. of Washington, Seattle, Washington, 1972.

14. Wisconsin Department of Natural Resources. NR 101 File Reports, 1975.

15. Lagerwerff, J. V. and A. W. Specht. Contamination of Roadside Soil and Vegetation with Cadmium, Nickel, Lead and Zinc. Environ. Sci. Technol. 4:583-586, 1970.

16. Konrad, J. G. and G. Chesters. Menomonee River Pilot Watershed Study; Summary Pilot Watershed Report. Submitted to PLUARG Task Group C (U.S.), Activity 2. Windsor, Ontario, May 1978.

17. U.S. Geological Survey. Water Resources Data for Wisconsin, Water Year 1976. U.S. Geological Survey, Madison, Wisconsin, 1977. pp. 144-177.

18. Armstrong, D. E., J. R. Perry and D. E. Flatness. Availability of Pollutants Associated with Suspended or Settled River Sediments which Gain Access to the Great Lakes. Final Report of the Menomonee River Pilot Watershed Study, Vol. 11, U.S. Environmental Protection Agency, 1979.

19. Pitt, R. Demonstration of Nonpoint Pollution Abatement through Improved Street Cleaning Practices. U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Cincinnati, Ohio, 1979.

20. Bowden, R. J. A Study to Develop Guidelines for the Evaluation of Harbor Sediments. Great Lakes Surveillance Branch, U.S. Environmental Protection Agency, Region V. Chicago, Illinois, 1976. Unpublished report.

21. Harris, R. F., G. Chesters and O. N. Allen. Dynamics of Soil Aggregation. Adv. in Agron. 18:107-169, 1966.

22. Wischmeier, W. H., C. B. Johnson and B. V. Cross. A Soil Erodibility Nomograph for Farmland and Construction Sites. J. Soil Water Conservation 26:189-193, 1971.

23. Wischmeier, W. H. and D. D. Smith. Predicting Rainfall Erosion Losses--A Guide to Conservation Planning. U.S. Department of Agriculture Handbook No. 537, 1978.

24. Wischmeier, W. H. Soil Erodibility by Rainfall and Runoff. In: Erosion: Research Techniques, Erodibility and Sediment Delivery. T. J. Toy (ed.). Geo Abstract Ltd., Norwich, England, 1977.

25. Kinniburgh, D. G., M. L. Jackson and J. K. Syers. Adsorption of Alkaline Earth, Transition and Heavy Metal Cations by Hydrous Oxide Gels of Iron and Aluminum. Soil Sci. Soc. Amer. Proc. 40:769-779, 1976.

26. Stumm, W. and J. J. Morgan. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. Wiley-Interscience, New York, N.Y., 1970. pp. 168, 484.